IN-46

NASA
Reference
Publication
1399

February
1997

Present State of Knowledge of the Upper Atmosphere 1996: An Assessment Report

Report to Congress and the Environmental Protection Agency

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Reply to Attn of:

April, 1997

With reference to: NASA Reference Publication 1399, *Present State of Knowledge of the Upper Atmosphere 1996: An Assessment Report,* we have enclosed a label with corrected information for the front cover of your Report. Please affix the label over the information shown below the title which lists the contributing scientists to this Report.

We apologize for any inconvenience.

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PREFACE

NASA has relied heavily on the entire scientific community, national and international, in its effort to provide a better understanding of the upper atmosphere and its perturbation in response to natural phenomena and human activities. The lists of contributors to the individual sections in this report are given in Section I. We are indebted to those who gave their time and knowledge. Specifically, we would like to thank the investigators and collaborators for providing information on their specific tasks. We also thank Rose Kendall and Kathy Wolfe for compiling the report and providing editorial support.

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SECTION A

INTRODUCTION

In compliance with the Clean Air Act Amendments of 1990, Public Law 101-549, the National Aeronautics and Space Administration (NASA) has prepared this report on the state of our knowledge of the Earth's upper atmosphere, and particularly, of the stratospheric ozone layer. This 1996 Report presents new findings since the last report in 1993 and is printed in two parts. Part I (Research Summaries) summarizes the objectives, status, and accomplishments of the research tasks supported under NASA's Upper Atmosphere Research Program (UARP) and Atmospheric Chemistry Modeling and Analysis Program (ACMAP) for the period of 1994-1996. Part II (this document) is a compilation of several scientific assessments, reviews, and summaries. Section B (Scientific Assessment of Ozone Depletion: 1994) and Section C (1995 Scientific Assessment of the Atmospheric Effects of Stratospheric Aircraft) are summaries of the most recent assessments of our current understanding of the chemical composition and the physical structure of the stratosphere, with particular emphasis on how the abundance and distribution of ozone is predicted to change in the future. Section D (ATLAS End-of-Series Statement), Section E (ASHOE/MAESA End-of-Mission Statement), and Section F (TOTE/VOTE End-of-Mission Statement) describe the scientific results for one Space Shuttle-based and two aircraft-based measurement campaigns, respectively. Section G (Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling) highlights the latest of NASA's biennial reviews of this important aspect of the atmospheric sciences. Section H (Atmospheric Ozone Research) presents a plan for the future direction of NASA's research program related to ozone and the broader area of atmospheric chemistry. This section also serves as the context for viewing how the work described in previous sections fits into the international suite of activities designed to better understand ozone and atmospheric chemistry. It also shows the relationship between ozone studies and other areas of NASA's research such as climate change.

For over two decades, scientists have postulated that certain pollutants directly associated with human activity could cause harmful effects by reducing the amount of stratospheric ozone. Initial concerns focused on supersonic aircraft emissions of NO and NO_2, and then shifted to the issue of chlorine loading of the stratosphere from chlorofluorocarbons (CFCs). Now there is compelling evidence that human activity can, in fact, change the atmospheric environment on a global scale. In recognition of the importance of understanding such perturbations, Congress directed NASA in June 1975 to "develop and carry out a comprehensive program of research, technology, and monitoring of the phenomena of the upper atmosphere so as to provide for an understanding of and to maintain the chemical and physical integrity of Earth's upper atmosphere."

Responding to this Congressional mandate, NASA implemented a long-range scientific research program, conducted through UARP and ACMAP, aimed at developing a comprehensive understanding of processes in the upper atmosphere. Additional activities are carried out through the NASA space flight programs. In the near-term, NASA has the responsibility of providing

triennial reports to Congress and concerned regulatory agencies on the status of upper atmospheric research, including scientific assessments of potential effects of human activities on the atmosphere, and particularly, on stratospheric ozone.

Many governments around the world, including the United States, have recognized that the ozone layer must be protected in order to preserve human health and aquatic and terrestrial ecosystems from damage due to enhanced levels of ultraviolet radiation. In particular, it was recognized that the use of chemicals containing chlorine (in the form of CFCs, hydrochlorofluorocarbons (HCFCs), and other chlorinated hydrocarbons such as methyl chloroform and carbon tetrachloride) and bromine (mainly in the form of halons and methyl bromide) constitute a potential threat to the ozone layer. More than twenty nations, including the United States, signed the Vienna Convention for the Protection of the Ozone Layer in Vienna, Austria, in 1985, and the Montreal Protocol on Substances That Deplete the Ozone Layer, in Montreal, Canada, in 1987. Subsequent amendments (London, UK, 1990; Copenhagen, Denmark, 1992; and Vienna, Austria, 1995) strengthened the Montreal Protocol by calling for an accelerated CFC phase-out schedule and added to the list of regulated compounds.

The Vienna Convention and the Montreal Protocol both call for all regulatory decisions to be based on a scientific understanding of the issues, and the Montreal Protocol specifically called for international scientific assessments at least every four years. The 1994 scientific assessment was coordinated by NASA, the National Oceanic and Atmospheric Administration (NOAA), the United Kingdom Department of the Environment (DOE), the United Nations Environment Program (UNEP), and the World Meteorological Organization (WMO). The executive summary and scientific summaries of the assessment chapters are reproduced in Section B.

The environmental impact of a proposed fleet of high-speed (i. e., supersonic) civil transport (HSCT) aircraft on the ozone layer is also being assessed. An interim assessment report from NASA's High-Speed Research Program, an element of the Atmospheric Effects of Aviation Project, was issued in January 1995, and the executive summary from this assessment report is included as Section C of this document. The possible impact of the entire range of effluents from such aircraft was considered using improved assessment models and detailed fleet emission scenarios. In addition, the major areas of scientific uncertainty were identified and quantified where possible. The emphasis of the 1995 report was on the effects of NO_x and H_2O on the atmospheric ozone content, as well as ozone changes due to increased particle surface area caused by aircraft effluents; concern over the latter issue arose due to the recently recognized importance of heterogeneous chemistry.

Process studies conducted via field campaigns, involving focused measurements within a particular atmospheric region so that specific chemical and physical processes can be understood and theories can be quantitatively tested, are fundamental to the assessment process. Such campaigns rely extensively on *in situ* and remote-sensing aircraft measurements as well as those from ground-, balloon-, and space-based instruments. Section D summarizes the scientific results of the Atmospheric Laboratory for Applications and Science (ATLAS), a series of three space Shuttle missions designed to measure the trace constituent composition of the Earth's stratosphere and mesosphere, and the related quantities of total solar irradiance and spectrally resolved solar ultraviolet irradiance. Section E describes the results of the Airborne Southern Hemisphere Ozone Experiment and the Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/ MAESA) airborne field campaigns that set out to investigate the causes of year-round mid-latitude

ozone loss in the Southern Hemisphere. Section F is devoted to two other coupled airborne field campaigns, the Tropical Ozone Transport Experiment and the Vortex Ozone Transport Experiment (TOTE/VOTE), designed to study processes responsible for the exchange and mixing of tropical (TOTE) and high-latitude (VOTE) stratospheric air into the mid-latitudes.

Also fundamental to the assessment process is a solid quantitative foundation of laboratory-derived photochemical reaction rates for use in predictive models. The biennial review and evaluation of kinetic and photochemical data by the NASA Panel for Data Evaluation is an important unifying document for the atmospheric sciences community. It offers a standard reference database for atmospheric modeling (for both assessment and research) thereby providing a common focus for laboratory measurements and theoretical studies. The most recent recommendations of this panel are being published as a 1996 Report from the Jet Propulsion Laboratory, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation Number 12 of the NASA Panel for Data Evaluation,* and pertinent sections are included as Section G of this document.

Understanding the causes and consequences of changes in atmospheric ozone is an area of continuing priority within NASA's Office of Mission to Planet Earth (MTPE). This commitment applies to outstanding questions related to stratospheric ozone depletion as well as to the changing composition and physical properties of the upper troposphere, a region of the atmosphere that plays an important role in the area of climate change through its interactions with the stratosphere. Section H presents this aspect of the MTPE strategic research plan, the implementation of which continues to provide high-quality scientific data to the atmospheric sciences community and to policy-makers who use such information in making environmental decisions.

The contributors to all of the sections mentioned above are listed in Section I.

SECTION B

SCIENTIFIC ASSESSMENT OF OZONE DEPLETION: 1994
EXECUTIVE SUMMARY

RECENT MAJOR SCIENTIFIC FINDINGS AND OBSERVATIONS

The laboratory investigations, atmospheric observations, and theoretical and modeling studies of the past few years have provided a deeper understanding of the human-influenced and natural chemical changes in the atmosphere and their relation to the Earth's stratospheric ozone layer and radiative balance of the climate system. Since the last international scientific assessment of the state of understanding, there have been several key ozone-related findings, observations, and conclusions:

- **The atmospheric growth rates of several major ozone-depleting substances have slowed, demonstrating the expected impact of the Montreal Protocol and its Amendments and Adjustments.** The abundances of the chlorofluorocarbons (CFCs), carbon tetrachloride, methyl chloroform, and halons in the atmosphere have been monitored at global ground-based sites since about 1978. Over much of that period, the annual growth rates of these gases have been positive. However, the data of recent years clearly show that the growth rates of CFC-11, CFC-12, halon-1301, and halon-1211 are slowing down. In particular, total tropospheric organic chlorine increased by only about 60 ppt/year (1.6%) in 1992, compared to 110 ppt/year (2.9%) in 1989. Furthermore, tropospheric bromine in halons increased by only about 0.25 ppt/year in 1992, compared to about 0.85 ppt/year in 1989. The abundance of carbon tetrachloride is actually decreasing. The observed trends in total tropospheric organic chlorine are consistent with reported production data, suggesting less emission than the maximum allowed under the Montreal Protocol and its Amendments and Adjustments. Peak total chlorine/bromine loading in the troposphere is expected to occur in 1994, but the stratospheric peak will lag by about 3 - 5 years. Since the stratospheric abundances of chlorine and bromine are expected to continue to grow for a few more years, increasing global ozone losses are predicted (other things being equal) for the remainder of the decade, with gradual recovery in the 21st century.
- **The atmospheric abundances of several of the CFC substitutes are increasing, as anticipated.** With phaseout dates for the CFCs and other ozone-depleting substances now fixed by international agreements, several hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are being manufactured and used as substitutes. The atmospheric growth of some of these compounds (e.g., HCFC-22) has been observed for several years, and the growth rates of others (e.g., HCFC-142b and HCFC-141b) are now being monitored. Tropospheric chlorine in HCFCs increased by 5 ppt/year in 1989 and about 10 ppt/year in 1992.

- **Record low global ozone levels were measured over the past two years.** Anomalous ozone decreases were observed in the mid-latitudes of both hemispheres in 1992 and 1993. The Northern Hemispheric decreases were larger than those in the Southern Hemisphere. Globally, ozone values were 1 - 2% lower than would be expected from an extrapolation of the trend prior to 1991, allowing for solar-cycle and quasi-biennial-oscillation (QBO) effects. The 1994 global ozone levels are returning to values closer to those expected from the longer-term downward trend.

- **The stratosphere was perturbed by a major volcanic eruption.** The eruption of Mt. Pinatubo in 1991 led to a large increase in sulfate aerosol in the lower stratosphere throughout the globe. Reactions on sulfate aerosols resulted in significant, but temporary, changes in the chemical partitioning that accelerated the photochemical ozone loss associated with reactive hydrogen (HO_x), chlorine, and bromine compounds in the lower stratosphere in mid-latitudes and polar regions. Absorption of terrestrial and solar radiation by the Mt. Pinatubo aerosol resulted in a transitory rise of 1°C (globally averaged) in the lower-stratospheric temperature and also affected the distribution of ozone through circulation changes. The observed 1994 recovery of global ozone is qualitatively consistent with observed gradual reductions of the abundances of these volcanic particles in the stratosphere.

- **Downward trends in total-column ozone continue to be observed over much of the globe, but their magnitudes are underestimated by numerical models.** Decreases in ozone abundances of about 4 - 5% per decade at mid-latitudes in the Northern and Southern Hemispheres continue to be observed by both ground-based and satellite-borne monitoring instruments. At mid-latitudes, the losses continue to be much larger during winter/spring than during summer/fall in both hemispheres, and the depletion increases with latitude, particularly in the Southern Hemisphere. Little or no downward trends are observed in the tropics (20°N - 20°S). While the current two-dimensional stratospheric models simulate the observed trends quite well during some seasons and latitudes, they underestimate the trends by factors of up to three in winter/spring at mid- and high latitudes. Several known atmospheric processes that involve chlorine and bromine and that affect ozone in the lower stratosphere are difficult to model and have not been adequately incorporated into these models.

- **Observations have demonstrated that halogen chemistry plays a larger role in the chemical destruction of ozone in the mid-latitude lower stratosphere than expected from gas phase chemistry.** Direct *in situ* measurements of radical species in the lower stratosphere, coupled with model calculations, have quantitatively shown that the *in situ* photochemical loss of ozone due to (largely natural) reactive nitrogen (NO_x) compounds is smaller than that predicted from gas phase chemistry, while that due to (largely natural) HO_x compounds and (largely anthropogenic) chlorine and bromine compounds is larger than that predicted from gas phase chemistry. This confirms the key role of chemical reactions on sulfate aerosols in controlling the chemical balance of the lower stratosphere. These and other recent scientific findings strengthen the conclusion of the previous assessment that the weight of scientific evidence suggests that the observed middle- and high-latitude ozone losses are largely due to anthropogenic chlorine and bromine compounds.

- **The conclusion that anthropogenic chlorine and bromine compounds, coupled with surface chemistry on natural polar stratospheric particles, are the cause of polar ozone depletion has been further strengthened.** Laboratory studies have provided a greatly improved understanding of how the chemistry on the surfaces of ice, nitrate, and sulfate particles can increase the abundance of ozone-depleting forms of chlorine in the polar stratospheres. Furthermore, satellite and *in situ* observations of the abundances of reactive nitrogen and chlorine compounds have improved the explanation of the different ozone-altering properties of the Antarctic and Arctic.

- **The Antarctic ozone "holes" of 1992 and 1993 were the most severe on record.** The Antarctic ozone "hole" has continued to occur seasonally every year since its advent in the late-1970s, with the occurrences over the last several years being particularly pronounced. Satellite, balloon-borne, and ground-based monitoring instruments revealed that the Antarctic ozone "holes" of 1992 and 1993 were the biggest (areal extent) and deepest (minimum amounts of ozone overhead), with ozone being locally depleted by more than 99% between about 14 - 19 km in October, 1992 and 1993. It is likely that these larger-than-usual ozone depletions could be attributed, at least in part, to sulfate aerosols from Mt. Pinatubo increasing the effectiveness of chlorine- and bromine-catalyzed ozone destruction. A substantial Antarctic ozone "hole" is expected to occur each austral spring for many more decades because stratospheric chlorine and bromine abundances will approach the pre-Antarctic-ozone-"hole" levels (late-1970s) very slowly during the next century.

- **Ozone losses have been detected in the Arctic winter stratosphere, and their links to halogen chemistry have been established.** Studies in the Arctic lower stratosphere have been expanded to include more widespread observations of ozone and key reactive species. In the late-winter/early-spring period, additional chemical losses of ozone up to 15 - 20% at some altitudes are deduced from these observations, particularly in the winters of 1991/2 and 1992/3. Model calculations constrained by the observations are also consistent with these losses, increasing the confidence in the role of chlorine and bromine in ozone destruction. The interannual variability in the photochemical and dynamical conditions of the Arctic polar vortex continues to limit the ability to predict ozone changes in future years.

- **The link between a decrease in stratospheric ozone and an increase in surface ultraviolet (UV) radiation has been further strengthened.** Measurements of UV radiation at the surface under clear-sky conditions show that low overhead ozone yields high UV radiation and in the amount predicted by radiative-transfer theory. Large increases of surface UV are observed in Antarctica and the southern part of South America during the period of the seasonal ozone "hole." Furthermore, elevated surface UV levels at mid-to-high latitudes were observed in the Northern Hemisphere in 1992 and 1993, corresponding to the low ozone levels of those years. However, the lack of a decadal (or longer) record of accurate monitoring of surface UV levels and the variation introduced by clouds and other factors have precluded the unequivocal identification of a long-term trend in surface UV radiation.

- **Methyl bromide continues to be viewed as a significant ozone-depleting compound.** Increased attention has been focused upon the ozone-depleting role of methyl bromide. Three potentially major anthropogenic sources of atmospheric methyl bromide have been identified (soil fumigation, biomass burning, and the exhaust of automobiles using leaded gasoline), in addition to the natural oceanic source. Recent laboratory studies have confirmed

the fast rate for the BrO + HO_2 reaction and established a negligible reaction pathway producing HBr, both of which imply greater ozone losses due to emissions of compounds containing bromine. While the magnitude of the atmospheric photochemical removal is well understood, there are significant uncertainties in quantifying the oceanic sink for atmospheric methyl bromide. The best estimate for the overall lifetime of atmospheric methyl bromide is 1.3 years, with a range of 0.8 - 1.7 years. The Ozone Depletion Potential (ODP) for methyl bromide is calculated to be about 0.6 (relative to an ODP of 1 for CFC-11).

- **Stratospheric ozone losses cause a global-mean negative radiative forcing.** In the 1991 scientific assessment, it was pointed out that the global ozone losses that were occurring in the lower stratosphere caused this region to cool and result in less radiation reaching the surface-troposphere system. Recent model studies have strengthened this picture. A long-term global-mean cooling of the lower stratosphere of between 0.25 and 0.4°C/decade has been observed over the last three decades. Calculations indicate that, on a global mean, the ozone losses between 1980 and 1990 offset about 20% of the radiative forcing due to the well-mixed greenhouse-gas increases during that period (i.e., carbon dioxide, methane, nitrous oxide, and halocarbons).

- **Tropospheric ozone, which is a greenhouse gas, appears to have increased in many regions of the Northern Hemisphere.** Observations show that tropospheric ozone, which is formed by chemical reactions involving pollutants, has increased above many locations in the Northern Hemisphere over the last 30 years. However, in the 1980s, the trends were variable, being small or nonexistent. In the Southern Hemisphere, there are insufficient data to draw strong inferences. At the South Pole, a decrease has been observed since the mid-1980s. Model simulations and limited observations suggest that tropospheric ozone has increased in the Northern Hemisphere since pre-industrial times. Such changes would augment the radiative forcing from all other greenhouse gases by about 20% over the same time period.

- **The atmospheric residence times of the important ozone-depleting gases, CFC-11 and methyl chloroform, and the greenhouse gas, methane, are now better known.** A reconciliation of observed concentrations with known emissions using an atmospheric model has led to a best-estimate lifetime of 50 years for CFC-11 and 5.4 years for methyl chloroform, with uncertainties of about 10%. These lifetimes provide an accurate standard for gases destroyed only in the stratosphere (such as CFCs and nitrous oxide) and for those also reacting with tropospheric hydroxyl radical, OH (such as HCFCs and HFCs), respectively. Recent model simulations of methane perturbations and a theoretical analysis of the tropospheric chemical system that couples methane, carbon monoxide, and OH have demonstrated that methane perturbations decay with a lengthened time scale in a range of about 12 - 17 years, as compared with the 10-year lifetime derived from the total abundance and losses. This longer response time and other indirect effects increase the estimate of the effectiveness of emissions of methane as a greenhouse gas by a factor of about two compared to the direct-effect-only values given in the 1991 assessment.

SUPPORTING SCIENTIFIC EVIDENCE AND RELATED ISSUES

Ozone Changes in the Tropics and Mid-Latitudes and Their Interpretation

- Analysis of global total-column ozone data through early 1994 shows substantial decreases of ozone in all seasons at mid-latitudes (30° - 60°) of both hemispheres. For example, in the middle latitudes of the Northern Hemisphere, downward trends of about 6% per decade over 1979 - 1994 were observed in winter and spring and about 3% per decade were observed in summer and fall. In the Southern Hemisphere, the seasonal difference was somewhat less, but the mid-latitude trends averaged a similar 4% to 5% per decade. There are no statistically significant trends in the tropics (20°S - 20°N). Trends through 1994 are about 1% per decade more negative in the Northern Hemisphere (2% per decade in the mid-latitude winter/spring in the Northern Hemisphere) compared to those calculated without using data after May 1991. At Northern mid-latitudes, the downward trend in ozone between 1981 - 1991 was about 2% per decade greater compared to that of the period 1970 - 1980.

- Satellite and ozonesonde data show that much of the downward trend in ozone occurs below 25 km (i.e., in the lower stratosphere). For the region 20 - 25 km, there is good agreement between the trends from the Stratospheric Aerosol and Gas Experiment (SAGE I/II) satellite instrument data and those from ozonesondes, with an observed annual-average decrease of 7 ± 4% per decade from 1979 to 1991 at 30° - 50°N latitude. Below 20 km, SAGE yields negative trends as large as 20 ± 8% per decade at 16 - 17 km, while the average of available mid-latitude ozonesonde data shows smaller negative trends of 7 ± 3% per decade. Integration of the ozonesonde data yields total-ozone trends consistent with total-ozone measurements. In the 1980s, upper-stratospheric (35 - 45 km) ozone trends determined by the data from SAGE I/II, Solar Backscatter Ultraviolet satellite spectrometer (SBUV), and the Umkehr method agree well at mid-latitudes, but less so in the tropics. Ozone declined 5 - 10% per decade at 35 - 45 km between 30°- 50°N and slightly more at southern mid-latitudes. In the tropics at 45 km, SAGE I/II and SBUV yield downward trends of 10 and 5% per decade, respectively.

- Simultaneous *in situ* measurements of a suite of reactive chemical species have directly confirmed modeling studies implying that the chemical destruction of ozone in the mid-latitude lower stratosphere is more strongly influenced by HO_x and halogen chemistry than NO_x chemistry. The seasonal cycle of ClO in the lower stratosphere at mid-latitudes in both hemispheres supports a role for *in situ* heterogeneous perturbations (i.e., on sulfate aerosols), but does not appear consistent with the timing of vortex processing or dilution. These studies provide key support for the view that sulfate aerosol chemistry plays an important role in determining mid-latitude chemical ozone destruction rates.

- The model-calculated ozone depletions in the upper stratosphere for 1980 - 1990 are in broad agreement with the measurements. Although these model-calculated ozone depletions did not consider radiative feedbacks and temperature trends, including these effects is not likely to reduce the predicted ozone changes by more than 20%.

- Models including the chemistry involving sulfate aerosols and polar stratospheric clouds (PSCs) better simulate the observed total ozone depletions of the past decade than models that include only gas phase reactions. However, they still underestimate the ozone loss by factors ranging from 1.3 to 3.0.

- Some unresolved discrepancies between observations and models exist for the partitioning of inorganic chlorine species, which could impact model predictions of ozone trends. These occur for the ClO/HCl ratio in the upper stratosphere and the fraction of HCl to total inorganic chlorine in the lower stratosphere.
- The transport of ozone-depleted air from polar regions has the potential to influence ozone concentrations at middle latitudes. While there are uncertainties about the importance of this process relative to *in situ* chemistry for mid-latitude ozone loss, both directly involve ozone destruction by chlorine- and bromine-catalyzed reactions.
- Radiosonde and satellite data continue to show a long-term cooling trend in globally annual-average lower-stratospheric temperatures of about 0.3 - 0.4°C per decade over the last three decades. Models suggest that ozone depletion is the major contributor to this trend.
- Anomalously large downward ozone trends have been observed in mid-latitudes of both hemispheres in 1992 and 1993 (i.e., the first two years after the eruption of Mt. Pinatubo), with Northern-Hemispheric decreases larger than those of the Southern Hemisphere. Global-average total-ozone levels in early 1993 were about 1% to 2% below that expected from the long-term trend and the particular phase of the solar and QBO cycles, while peak decreases of about 6 - 8% from expected ozone levels were seen over 45 - 60°N. In the first half of 1994, ozone levels returned to values closer to those expected from the long-term trend.
- The sulfur gases injected by Mt. Pinatubo led to large enhancements in stratospheric sulfate aerosol surface areas (by a maximum factor of about 30 - 40 at northern mid-latitudes within a year after the eruption), which have subsequently declined.
- Anomalously low ozone was measured at altitudes below 25 km at a Northern-Hemispheric mid-latitude station in 1992 and 1993 and was correlated with observed enhancements in sulfate-aerosol surface areas, pointing towards a causal link.
- Observations indicate that the eruption of Mt. Pinatubo did not significantly increase the HCl content of the stratosphere.
- The recent large ozone changes at mid-latitudes are highly likely to have been due, at least in part, to the greatly increased sulfate aerosol in the lower stratosphere following Mt. Pinatubo. Observations and laboratory studies have demonstrated the importance of heterogeneous hydrolysis of N_2O_5 on sulfate aerosols in the atmosphere. Evidence suggests that $ClONO_2$ hydrolysis also occurs on sulfate aerosols under cold conditions. Both processes perturb the chemistry in such a way as to increase ozone loss through coupling with the anthropogenic chlorine and bromine loading of the stratosphere.
- Global mean lower stratospheric temperatures showed a marked transitory rise of about 1°C following the eruption of Mt. Pinatubo in 1991, consistent with model calculations. The warming is likely due to absorption of radiation by the aerosols.

Polar Ozone Depletion

- In 1992 and 1993, the biggest-ever (areal extent) and deepest-ever (minimum ozone below 100 Dobson units) ozone "holes" were observed in the Antarctic. These extreme ozone depletions may have been due to the chemical perturbations caused by sulfate aerosols from Mt. Pinatubo, acting in addition to the well-recognized chlorine and bromine reactions on polar stratospheric clouds.
- Recent results of observational and modeling studies reaffirm the role of anthropogenic halocarbon species in Antarctic ozone depletion. Satellite observations show a strong spatial and temporal correlation of ClO abundances with ozone depletion in the Antarctic vortex. In the Arctic winter, a much smaller ozone loss has been observed. These losses are both consistent with photochemical model calculations constrained with observations from *in situ* and satellite instruments.
- Extensive new measurements of HCl, ClO, and $ClONO_2$ from satellites and *in situ* techniques have confirmed the picture of the chemical processes responsible for chlorine activation in polar regions and the recovery from those processes, strengthening current understanding of the seasonal cycle of ozone depletion in both polar regions.
- New laboratory and field studies strengthen the confidence that reactions on sulfate aerosols can activate chlorine under cold conditions, particularly those in the polar regions. Under volcanically perturbed conditions when aerosols are enhanced, these processes also likely contribute to ozone losses at the edges of PSC formation regions (both vertical and horizontal) just outside of the southern vortex and in the Arctic.
- Satellite measurements have confirmed that the Arctic vortex is much less denitrified than the Antarctic, which is likely to be an important factor in determining the interhemispheric differences in polar ozone loss.
- Interannual variability in the photochemical and dynamical conditions of the vortices limits reliable predictions of future ozone changes in the polar regions, particularly in the Arctic.

Coupling Between Polar Regions and Mid-Latitudes

- Recent satellite observations of long-lived tracers and modeling studies confirm that, above 16 km, air near the center of the polar vortex is substantially isolated from lower latitudes, especially in the Antarctic.
- Erosion of the vortex by planetary-wave activity transports air from the vortex-edge region to lower latitudes. Nearly all observational and modeling studies are consistent with a time scale of 3 - 4 months to replace a substantial fraction of Antarctic vortex air. The importance of this transport to *in situ* chemical effects for mid-latitude ozone loss remains poorly known.
- Air is readily transported between polar regions and mid-latitudes below 16 km. The influence of this transport on mid-latitude ozone loss has not been quantified.

Tropospheric Ozone

- There is observational evidence that tropospheric ozone (about 10% of the total-column ozone) has increased in the Northern Hemisphere (north of 20°N) over the past three decades. The upward trends are highly regional. They are smaller in the 1980s than in the 1970s and may be slightly negative at some locations. European measurements at surface sites also indicate a doubling in the lower-tropospheric ozone concentrations since earlier this century. At the South Pole, a decrease has been observed since the mid-1980s. Elsewhere in the Southern Hemisphere, there are insufficient data to draw strong inferences.
- There is strong evidence that ozone levels in the boundary layer over the populated regions of the Northern Hemisphere are enhanced by more than 50% due to photochemical production from anthropogenic precursors, and that export of ozone from North America is a significant source for the North Atlantic region during summer. It has also been shown that biomass burning is a significant source of ozone (and carbon monoxide) in the tropics during the dry season.
- An increase in UV-B radiation (e.g., from stratospheric ozone loss) is expected to decrease tropospheric ozone in the background atmosphere, but, in some cases, it will increase production of ozone in the more polluted regions.
- Model calculations predict that a 20% increase in methane concentrations would result in tropospheric ozone increases ranging from 0.5 to 2.5 ppb in the tropics and the northern mid-latitude summer, and an increase in the methane residence time to about 14 years (a range of 12 - 17 years). Although there is a high degree of consistency in the global transport of short-lived tracers within three-dimensional chemical-transport models, and a general agreement in the computation of photochemical rates affecting tropospheric ozone, many processes controlling tropospheric ozone are not adequately represented or tested in the models, hence limiting the accuracy of these results.

Trends in Source Gases Relating to Ozone Changes

- CFCs, carbon tetrachloride, methyl chloroform, and the halons are major anthropogenic source gases for stratospheric chlorine and bromine, and hence stratospheric ozone destruction. Observations from several monitoring networks worldwide have demonstrated slowdowns in growth rates of these species that are consistent (except for carbon tetrachloride) with expectations based upon recent decreases in emissions. In addition, observations from several sites have revealed accelerating growth rates of the CFC substitutes, HCFC-22, HCFC-141b, and HCFC-142b, as expected from their increasing use.
- Methane levels in the atmosphere affect tropospheric and stratospheric ozone levels. Global methane increased by 7% over about the past decade. However, the 1980s were characterized by slower growth rates, dropping from approximately 20 ppb per year in 1980 to about 10 ppb per year by the end of the decade. Methane growth rates slowed dramatically in 1991 and 1992, but the very recent data suggest that they have started to increase in late 1993. The cause(s) of this behavior are not known, but it is probably due to changes in methane sources rather than sinks.

- Despite the increased methane levels, the total amount of carbon monoxide in today's atmosphere is less than it was a decade ago. Recent analyses of global carbon monoxide data show that tropospheric levels grew from the early 1980s to about 1987 and have declined from the late 1980s to the present. The cause(s) of this behavior have not been identified.

Consequences of Ozone Changes

- The only general circulation model (GCM) simulation to investigate the climatic impacts of observed ozone depletions between 1970 and 1990 supports earlier suggestions that these depletions reduced the model-predicted warming due to well-mixed greenhouse gases by about 20%. This is consistent with radiative forcing calculations.
- Model simulations suggest that increases in tropospheric ozone since pre-industrial times may have made significant contributions to the greenhouse forcing of the Earth's climate system, enhancing the current total forcing by about 20% compared to that arising from the changes in the well-mixed greenhouses gases over that period.
- Large increases in ultraviolet (UV) radiation have been observed in association with the ozone hole at high southern latitudes. The measured UV enhancements agree well with model calculations.
- Clear-sky UV measurements at mid-latitude locations in the Southern Hemisphere are significantly larger than at a corresponding site in the Northern Hemisphere, in agreement with expected differences due to ozone column and Sun-Earth separation.
- Local increases in UV-B were measured in 1992/93 at mid- and high latitudes in the Northern Hemisphere. The spectral signatures of the enhancements clearly implicate the anomalously low ozone observed in those years, rather than variability of cloud cover or tropospheric pollution. Such correlations add confidence to the ability to link ozone changes to UV-B changes over relatively long time scales.
- Increases in clear-sky UV over the period 1979 to 1993 due to observed ozone changes are calculated to be greatest at short wavelengths and at high latitudes. Poleward of 45°, the increases are greatest in the Southern Hemisphere.
- Uncertainties in calibration, influence of tropospheric pollution, and difficulties of interpreting data from broad-band instruments continue to preclude the unequivocal identification of long-term UV trends. However, data from two relatively unpolluted sites do appear to show UV increases consistent with observed ozone trends. Given the uncertainties of these studies, it now appears that quantification of the natural (i.e., pre-ozone-reduction) UV baseline has been irrevocably lost at mid- and high latitudes.
- Scattering of UV radiation by stratospheric aerosols from the Mt. Pinatubo eruption did not alter total surface-UV levels appreciably.

Related Phenomena and Issues

METHYL BROMIDE

- Three potentially major anthropogenic sources of methyl bromide have been identified: (i) soil fumigation: 20 to 60 ktons per year, where new measurements reaffirm that about 50% (ranging from 20 - 90%) of the methyl bromide used as a soil fumigant is released into the atmosphere; (ii) biomass burning: 10 to 50 ktons per year; and (iii) the exhaust of automobiles using leaded gasoline: 0.5 to 1.5 ktons per year or 9 to 22 ktons per year (the two studies report emission factors that differ by a factor of more than 10). In addition, the one known major natural source of methyl bromide is oceanic, with emissions of 60 to 160 ktons per year.
- Recent measurements have confirmed that there is more methyl bromide in the Northern Hemisphere than in the Southern Hemisphere, with an interhemispheric ratio of 1.3.
- There are two known sinks for atmospheric methyl bromide: (i) atmospheric, with a lifetime of 2.0 years (1.5 to 2.5 years); and (ii) oceanic, with an estimated lifetime of 3.7 years (1.5 to 10 years). The overall best estimate for the lifetime of atmospheric methyl bromide is 1.3 years, with a range of 0.8 to 1.7 years. An overall lifetime of less than 0.6 years is thought to be highly unlikely because of constraints imposed by the observed interhemispheric ratio and total known emissions.
- The chemistry of bromine-induced stratospheric ozone destruction is now better understood. Laboratory measurements have confirmed the fast rate for the $BrO + HO_2$ reaction and have established a negligible reaction pathway producing HBr, both of which imply greater ozone losses due to emissions of compounds containing bromine. Stratospheric measurements show that the abundance of HBr is less than 1 ppt.
- Bromine is estimated to be about 50 times more efficient than chlorine in destroying stratospheric ozone on a per-atom basis. The ODP for methyl bromide is calculated to be about 0.6, based on an overall lifetime of 1.3 years. An uncertainty analysis suggests that the ODP is unlikely to be less than 0.3.

AIRCRAFT

- Subsonics: Estimates indicate that present subsonic aircraft operations may be significantly increasing trace species (primarily NO_x, sulfur dioxide, and soot) at upper-tropospheric altitudes in the North-Atlantic flight corridor. Models indicate that the NO_x emissions from the current subsonic fleet produce upper-tropospheric ozone increases as much as several percent, maximizing at northern mid-latitudes. Since the results of these rather complex models depend critically on NO_x chemistry and since the tropospheric NO_x budget is uncertain, little confidence should be put in these quantitative model results at the present time.
- Supersonics: Atmospheric effects of supersonic aircraft depend on the number of aircraft, the altitude of operation, the exhaust emissions, and the background chlorine and aerosol loadings. Projected fleets of supersonic transports would lead to significant changes in trace-species concentrations, especially in the North-Atlantic flight corridor. Two-dimensional model calculations of the impact of a projected fleet (500 aircraft, each emitting 15 grams of NO_x per kilogram of fuel burned at Mach 2.4) in a stratosphere with a chlorine loading of 3.7 ppb,

imply additional (i.e., beyond those from halocarbon losses) annual-average ozone column decreases of 0.3 - 1.8% for the Northern Hemisphere. There are, however, important uncertainties in these model results, especially in the stratosphere below 25 km. The same models fail to reproduce the observed ozone trends in the stratosphere below 25 km between 1980 and 1990. Thus, these models may not be properly including mechanisms that are important in this crucial altitude range.

- Climate Effects: Reliable quantitative estimates of the effects of aviation emissions on climate are not yet available. Some initial estimates indicate that the climate effects of ozone changes resulting from subsonic aircraft emissions may be comparable to those resulting from their CO_2 emissions.

OZONE DEPLETION POTENTIALS (ODPS)

- If a substance containing chlorine or bromine decomposes in the stratosphere, it will destroy some ozone. HCFCs have short tropospheric lifetimes, which tends to reduce their impact on stratospheric ozone as compared to CFCs and halons. However, there are substantial differences in ODPs among various substitutes. The steady-state ODPs of substitute compounds considered in the present assessment range from about 0.01 - 0.1.
- Tropospheric degradation products of CFC substitutes will not lead to significant ozone loss in the stratosphere. Those products will not accumulate in the atmosphere and will not significantly influence the ODPs and Global Warming Potentials (GWPs) of the substitutes.
- Trifluoroacetic acid, formed in the atmospheric degradation of HFC-134a, HCFC-123, and HCFC-124, will enter into the aqueous environment, where biological, rather than physico-chemical, removal processes may be effective.
- It is known that atomic fluorine (F) itself is not an efficient catalyst for ozone loss, and it is concluded that the F-containing fragments from the substitutes (such as CF_3O_x) also have negligible impact on ozone. Therefore, ODPs of HFCs containing the CF_3 group (such as HFC-134a, HFC-23, and HFC-125) are likely to be much less than 0.001.
- New laboratory measurements and associated modeling studies have confirmed that perfluorocarbons and sulfur hexafluoride are long-lived in the atmosphere and act as greenhouse gases.
- The ODPs for several new compounds, such as HCFC-225ca, HCFC-225cb, and CF_3I, have been evaluated using both semi-empirical and modeling approaches, and are found to be 0.03 or less.

GLOBAL WARMING POTENTIALS (GWPS)

- Both the direct and indirect components of the GWP of methane have been estimated using model calculations. Methane's influence on the hydroxyl radical and the resulting effect on the methane response time lead to substantially longer response times for decay of emissions than OH removal alone, thereby increasing the GWP. In addition, indirect effects including production of tropospheric ozone and stratospheric water vapor were considered and are estimated to range from about 15 to 45% of the total GWP (direct plus indirect) for methane.

- GWPs, including indirect effects of ozone depletion, have been estimated for a variety of halocarbons, clarifying the relative radiative roles of ozone-depleting compounds (i.e., CFCs and halons). The net GWPs of halocarbons depend strongly upon the effectiveness of each compound for ozone destruction; the halons are highly likely to have negative net GWPs, while those of the CFCs are likely to be positive over both 20- and 100-year time horizons.

IMPLICATIONS FOR POLICY FORMULATION

The research findings of the past few years that are summarized above have several major implications as scientific input to governmental, industrial, and other policy decisions regarding human-influenced substances that lead to depletion of the stratospheric ozone layer and to changes of the radiative forcing of the climate system:

- **The Montreal Protocol and its Amendments and Adjustments are reducing the impact of anthropogenic halocarbons on the ozone layer and should eventually eliminate this ozone depletion.** Based on assumed compliance with the amended Montreal Protocol *(Copenhagen, 1992)* by all nations, the stratospheric chlorine abundances will continue to grow from their current levels (3.6 ppb) to a peak of about 3.8 ppb around the turn of the century. The future total bromine loading will depend upon choices made regarding future human production and emissions of methyl bromide. After around the turn of the century, the levels of stratospheric chlorine and bromine will begin a decrease that will continue into the 21st and 22nd centuries. The rate of decline is dictated by the long residence times of the CFCs, carbon tetrachloride, and halons. Global ozone losses and the Antarctic ozone "hole" were first discernible in the late 1970s and are predicted to recover in about the year 2045, other things being equal. The recovery of the ozone layer would have been impossible without the Amendments and Adjustments to the original Protocol *(Montreal, 1987)*.

- **Peak global ozone losses are expected to occur during the next several years.** The ozone layer will be most affected by human-influenced perturbations and susceptible to natural variations in the period around the year 1998, since the peak stratospheric chlorine and bromine abundances are expected to occur then. Based on extrapolation of current trends, observations suggest that the maximum ozone loss, relative to the late 1960s, will likely be:

  (i) about 12 - 13% at Northern mid-latitudes in winter/spring (i.e., about 2.5% above current levels);

  (ii) about 6 - 7% at Northern mid-latitudes in summer/fall (i.e., about 1.5% above current levels); and

  (iii) about 11% (with less certainty) at Southern mid-latitudes on a year-round basis (i.e., about 2.5% above current levels).

  Such changes would be accompanied by 15%, 8%, and 13% increases, respectively, in surface erythemal radiation, if other influences such as clouds remain constant. Moreover, if there were to be a major volcanic eruption like that of Mt. Pinatubo, or if an extremely cold and persistent Arctic winter were to occur, then the ozone losses and UV increases could be larger in individual years.

- **Approaches to lowering stratospheric chlorine and bromine abundances are limited.** Further controls on ozone-depleting substances would not be expected to significantly change the timing or the magnitude of the peak stratospheric halocarbon abundances and hence peak ozone loss. However, there are four approaches that would steepen the initial fall from the peak halocarbon levels in the early decades of the next century:

  (i) If emissions of methyl bromide from agricultural, structural, and industrial activities were to be eliminated in the year 2001, then the integrated effective future chlorine loading above the 1980 level (which is related to the cumulative future loss of ozone) is predicted to be 13% less over the next 50 years relative to full compliance to the Amendments and Adjustments to the Protocol.

  (ii) If emissions of HCFCs were to be totally eliminated by the year 2004, then the integrated effective future chlorine loading above the 1980 level is predicted to be 5% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.

  (iii) If halons presently contained in existing equipment were never released to the atmosphere, then the integrated effective future chlorine loading above the 1980 level is predicted to be 10% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.

  (iv) If CFCs presently contained in existing equipment were never released to the atmosphere, then the integrated effective future chlorine loading above the 1980 level is predicted to be 3% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.

- **Failure to adhere to the international agreements will delay recovery of the ozone layer.** If there were to be additional production of CFCs at 20% of 1992 levels for each year through 2002 and ramped to zero by 2005 (beyond that allowed for countries operating under Article 5 of the Montreal Protocol), then the integrated effective future chlorine loading above the 1980 level is predicted to be 9% more over the next 50 years relative to full compliance to the Amendments and Adjustments to the Protocol.

- **Many of the substitutes for the CFCs and halons are also notable greenhouse gases.** Several CFC and halon substitutes are not addressed under the Montreal Protocol (because they do not deplete ozone), but, because they are greenhouse gases, fall under the purview of the Framework Convention on Climate Change. There is a wide range of values for the Global Warming Potentials (GWPs) of the HFCs (150 - 10000), with about half of them having values comparable to the ozone-depleting compounds they replace. The perfluorinated compounds, some of which are being considered as substitutes, have very large GWPs (e.g., 5000 - 10000). These are examples of compounds whose current atmospheric abundances are relatively small, but are increasing or could increase in the future.

- **Consideration of the ozone change will be one necessary ingredient in understanding climate change.** The extent of our ability to attribute any climate change to specific causes will likely prove to be important scientific input to decisions regarding predicted human-induced influences on the climate system. Changes in ozone since pre-industrial times as a result of human activity are believed to have been a significant influence on radiative forcing; this human influence is expected to continue into the foreseeable future.

SCIENTIFIC ASSESSMENT OF OZONE DEPLETION: 1994
CHAPTER SUMMARIES

CHAPTER 1: OZONE MEASUREMENTS

The quality of the total ozone measurements made by ground-based and satellite systems has been assessed and trends calculated where appropriate.

- Trends in total ozone since 1979 have been updated through early 1994:
  - Northern Hemisphere middle latitude trends are significantly negative in all seasons, but are much larger in winter/spring (about 6%/decade), than in summer/fall (about 3%/decade).
  - Tropical (approximately 20°S to 20°N) trends are slightly negative, but not statistically significant when suspected drift in the satellite data is incorporated into the uncertainty.
  - Southern mid-latitude trends are significantly negative in all seasons, and increase in magnitude for high latitudes.
- Representative trends (annual averages, in % per decade) for north and south mid-latitudes and the tropics are as follows.

		Latitude					
		Mid South		Equatorial		Mid North	
Recent: 1/79 to 5/94	SBUV+SBUV/2	-4.9	± 1.5	-1.8	± 1.4	-4.6	± 1.8
1/79 to 2/94	Dobson network	-3.2	± 1.3	-1.1	± 0.6	-4.8	± 0.8
1/79 to 2/94	Ozonometer (former USSR)	na		na		-4.9	± 0.8
Pre-Pinatubo: 1/79 to 5/91	SBUV+SBUV/2	-4.9	± 2.3	-0.8	± 2.1	-3.3	± 2.4
1/79 to 5/91	TOMS	-4.5	± 2.1	+0.4	± 2.1	-4.0	± 2.1
1/79 to 5/91	Dobson network	-3.8	± 1.3	+0.2	± 1.2	-3.9	± 0.7
1/79 to 5/91	Ozonometer (former USSR)	na		na		-3.8	± 1.0

Note: uncertainties (±) are expressed at the 95% confidence limits (2 standard errors).

- The corresponding ozone loss (in %) accumulated over 15.3 years for trends calculated through 1994 are:

	Latitude					
	Mid South		Equatorial		Mid North	
SBUV+SBUV/2	-7.4	± 2.3	-2.7	± 2.2	-7.0	± 2.7
Dobson network	-4.8	± 2.1	-1.7	± 0.9	-7.3	± 1.3
Ozonometer (former USSR)	na		na		-7.5	± 1.3

- There was a statistically significant increase (about 2%/decade) in the average rate of ozone depletion at the Dobson stations north of 25°N in the period 1981 to 1991 compared to the period 1970 to 1980.
- We have confidence in the trends deduced from the ground-based network, particularly in the Northern Hemisphere. The record is longer than for the satellite instruments, although the geographic coverage is patchy, with most stations situated in the Northern Hemisphere mid-latitudes. The absolute calibration of the International Standard Dobson spectrophotometer has been maintained at ± 1%/decade. The quality of the data from the ground-based network has improved since the last assessment, partly as a result of improvements to the existing records and partly as a result of the improving quality control in the ground-based network.
- An extensive revision and reanalysis of the measurements made using the filter ozonometer data from the vast area of the former USSR has recently been performed. Trend estimates from these revised data substantiate those made at similar latitudes by Dobson and satellite instruments.
- During the 1980s, the Total Ozone Mapping Spectrometer (TOMS) total ozone calibration drifted by 1 to 2% relative to the Dobson instruments, depending on latitude. In addition, a systematic bias of 1 to 2%/decade may be present in measurements made at high solar zenith angles (and so is most important at high latitudes in winter). Our confidence in the trends presented in the 1991 Ozone Assessment, which covered the period through March 1991, is unchanged.
- However after this time, a problem developed in the TOMS instrument that lasted until the instrument became inoperative in May 1993. This problem resulted in systematic errors dependent on both season and latitude, and caused, on average, a drift of 1 to 2% between 1991 and 1993. TOMS satellite measurements made after May 1991 were, therefore, not used for trend analyses. A TOMS instrument was launched on the Meteor-3 satellite in August 1991. The satellite orbit is not ideal and the measurements from this instrument have not yet been sufficiently assessed to allow use in trend analyses.

- The drift in the calibration of total ozone by the Solar Backscattered Ultraviolet (SBUV) instrument from January 1979 to June 1990 was 1% or less relative to Dobson instruments, and any seasonal differences in the Northern Hemisphere were less than 1%. The SBUV/2 instrument on board the NOAA-11 satellite has measurements available from January 1989. The drift relative to Dobson instruments in the Northern Hemisphere has been less than 1%. However, there is an apparent seasonal cycle in the differences of about 1 to 2% (minimum to maximum).
- Nearly all ground-based instruments are now on the calibration scale of the World Standard Dobson Instrument #83. The quality of the measurements made at individual stations is tested using satellite data; any revision of the data is based on available instrumental records. Satellite measurements are independently calibrated by checking the internal consistency. However, the satellite record is tested for possible drift by comparison with the collection of station data. Thus, the ground-based and satellite records are not completely independent from one another.

Trends in the Vertical Distribution of Ozone

The state of knowledge about the trends in the vertical distribution of ozone is not as good as that about the total ozone trends. The quality of the available data varies considerably with altitude.

- At altitudes of 35 to 45 km, there is reasonable agreement between the Stratospheric Aerosol and Gas Experiment I/II (SAGE I/II), SBUV, and Umkehr, that during 1979 to 1991, ozone declined 5 to 10% per decade at 30° to 50°N and slightly more at southern mid-latitudes. In the tropics, SAGE I/II gives larger trends (ca.-10% per decade) than SBUV (ca. -5% per decade) at these altitudes.
- At altitudes between 25 and 30 km, there is reasonable agreement between SAGE I/II, SBUV, Umkehr, and ozonesondes that, during the 1979 to 1991 period, there was no significant ozone depletion at any latitude. The agreement continues down to about 20 km, where statistically significant reductions of $7 \pm 4\%$ per decade were observed between 30° and 50°N by both ozonesondes and SAGE I/II. Over the longer period from 1968to 1991, the ozonesonde record indicates a trend of $-4 \pm 2\%$ per decade at 20 km at northern mid-latitudes.
- There appear to have been sizeable ozone reductions during the 1979 to 1991 period in the 15 to 20 km region in mid-latitudes. There is disagreement on the magnitude of the reduction, with SAGE indicating trends as large as $-20 \pm 8\%$ per decade at 16 to 17 km and the ozonesondes indicating an average trend of $-7 \pm 3\%$ per decade in the Northern Hemisphere. The trend in the integrated ozone column for SAGE is larger than those found from SBUV, TOMS, and the ground-based network, but the uncertainties are too large to evaluate the consistency between the datasets properly. For 1968 to 1991, the ozonesonde record indicates a trend of $-7 \pm 3\%$ per decade at 16 km at northern mid-latitudes.
- In the tropics, trend determination at altitudes between 15 and 20 km is made difficult by the small ozone amounts. In addition, the large vertical ozone gradients make the trends very sensitive to small vertical displacements of the profile. The SAGE I/II record indicates large (-20 to -30% (± 18%) per decade) trends in the 16 to 17 km region (-10% (± 8%) at 20 km). Limited tropical ozonesonde data sets at Natal, 6°S and Hilo, 20°N do not indicate significant trends between 16 and 17 km or at any other altitude for this time period. With currently

available information it is difficult to evaluate the trends below 20 km in the tropics, as the related uncertainties are large. The effect on the trend in the total column from any changes at these altitudes would be small.

- In the free troposphere, only limited data (all from ozonesondes) are available for trend determination. In the Northern Hemisphere, trends are highly variable between regions. Upward trends in the 1970s over Europe have declined significantly in the 1980s, have been small or non-existent over North America, and continue upward over Japan. The determination of the size of the change over North America requires a proper treatment of the relative tropospheric sensitivities for the type of sondes used during different time periods.
- Surface measurements indicate that ozone levels at the surface in Europe have doubled since the 1950s. Over the last two decades there has been a downward trend at the South Pole and positive trends are observed at high altitude sites in the Northern Hemisphere. When considering the latter conclusion, the regional nature of trends in the Northern Hemisphere must be borne in mind.

Observations of Ozone and Aerosols in 1991 to 1994

- Global total ozone values in 1992/93 were 3 to 4% lower than the 1980s average. If the trend, solar cycle, and quasi-biennial oscillation (QBO) effects inferred from the 1980s record are extrapolated, an additional global anomaly of between -1 and -2% remains.
- The most negative anomalies were observed in the Northern Hemisphere springs in 1992 and 1993, with peak deviations of 6 to 10% in February through April 1993.
- A reduction of 3 to 4% occurred in the tropics in the six months following the eruption of Mt. Pinatubo.
- Overall the smallest effects were observed in the extra-tropical Southern Hemisphere, where total ozone amounts were at the low end of the range observed in the 1980s, as would be expected from the long-term downward trend observed in that region.
- In 1994, global ozone levels are also at the low end of the 1980s range, again in line with expectations of a continuation of the observed long-term trend.
- Following the June 1991 eruption of Mt. Pinatubo, stratospheric aerosol levels increased globally, with northern mid-latitude peak particle surface areas increasing by factors of 30 to 40 above pre-eruption values about one year after the eruption. Since that time, they have been decreasing.
- Several mechanisms have been suggested as causes of the total ozone anomalies, though the relative importance is not yet clear. The possible influences include: radiative, dynamical and chemical perturbations resulting from the Mt. Pinatubo volcanic aerosol; and global and regional dynamical perturbations, including the El Niño-Southern Oscillation.

Antarctic Ozone Depletion

- Record low mean values for October were observed at three Antarctic ground-based stations with continuous records since the late 1950s and early 1960s. There is no evidence of major springtime ozone depletion in Antarctica at any of the 4 Dobson stations prior to 1980.

- In early October 1993, a record low daily value of total ozone of 91 ± 5 DU was observed with an ozonesonde at the South Pole. During this flight (and in several others), no detectable ozone (less than 1%) was found over a 5 km range from 14 to 19 km, implying that complete chemical destruction of ozone had occurred. The geographical extents of the ozone holes in 1992 and 1993 were the two largest on record.
- A comparison of ozonesonde measurements made at the South Pole from 1967 to 1971 with those made between 1986 and 1991 reaffirms that the Antarctic depletion that has developed since the early period occurs at altitudes between 14 and 20 km and that the largest changes occur in September, October, and November.

CHAPTER 2: SOURCE GASES: TRENDS AND BUDGETS

Tropospheric growth rates of the major anthropogenic source species for stratospheric chlorine and bromine (chlorofluorocarbons (CFCs), carbon tetrachloride, methyl chloroform, halons) have slowed significantly, in response to substantially reduced emissions required by the Montreal Protocol. Total tropospheric chlorine grew by about 60 pptv (1.6%) in 1992 compared to 110 pptv (2.9%) in 1989. Tropospheric bromine in the form of halons grew by 0.2-0.3 pptv in 1992, compared to 0.6-1.1 pptv in 1989.

Hydrochlorofluorocarbon (HCFC) growth rates are accelerating, as they are being used increasingly as CFC substitutes. Tropospheric chlorine as HCFCs increased in 1992 by about 10 pptv, thus accounting for about 15% of total tropospheric chlorine growth, compared to 5 pptv in 1989 (5% of tropospheric chlorine growth).

The atmospheric residence times of CFC-11 and methyl chloroform are now better known. Model studies simulating atmospheric abundances using more realistic emission amounts have led to best-estimated lifetimes of 50 years for CFC-11 and 5.4 years for methyl chloroform, with uncertainties of about 10%. These models, calibrated against CFC-11 and methyl chloroform, are used to calculate the lifetimes, and hence ODPs (Ozone Depletion Potentials), of other gases destroyed only in the stratosphere (other CFCs and nitrous oxide) and those reacting significantly with tropospheric hydroxyl radicals (HCFCs and hydrofluorocarbons (HFCs)).

Methyl chloride, released from the oceans (natural) and biomass burning (anthropogenic), is a significant source of tropospheric chlorine, contributing about 15% of the total tropospheric chlorine abundance in 1992 (3.8 ppbv). Data collected from the late 1970s to the mid-1980s showed no long-term trend. A paucity of published observational data since means that the likely existence of a global trend in this important species cannot be assessed further.

The total abundance of organic halocarbons in the lower stratosphere is well characterized by *in situ* and remote observations of individual species. Observed totals are consistent with abundances of primary species in the troposphere, suggesting that other source species are not important in the stratosphere. Loss of halocarbons is found as their residence time in the stratosphere increases, consistent with destruction by known photochemical processes. Since the loss of halocarbons produces inorganic chlorine and bromine species associated with ozone loss processes, these observations also constrain the abundance of these organic species in the lower stratosphere.

Volcanoes are an insignificant source of stratospheric chlorine. Satellite and aircraft observations of upper and lower stratospheric hydrochloric acid (HCl) are consistent with stratospheric chlorine being organic, largely anthropogenic, in origin. No significant increase in HCl was found in the stratosphere following the intense eruption of Mt. Pinatubo in 1991. Elevated HCl levels were detected in the eruption cloud of the El Chichón volcano in 1982, but no related change in global stratospheric HCl was observed.

The 1980s were characterized by declining global methane growth rates, being approximately 20 ppbv per year in 1980 declining approximately monotonically to 10 ppbv per year by the end of the decade. Methane growth rates slowed dramatically in 1991 to 1992, but probably started to increase in late 1993. During 1992 global methane levels grew by only 5 ppbv. The causes of this global anomaly (which manifested predominantly at high latitudes in the Northern Hemisphere) are not known with certainty, but are probably due to changes in methane sources rather than in methane sinks. Global growth rate anomalies have been observed in methane records in the 1920s and 1970s from air trapped in Antarctic ice.

Despite the increased methane levels, the total amount of carbon monoxide (CO) in today's atmosphere is less than it was a decade ago. Recent analyses of global CO data show that tropospheric levels grew from the early 1980s to about 1987 and have declined from the late 1980s to the present. The causes of this behavior have not been identified.

CHAPTER 3: POLAR OZONE

Substantial new results have been obtained since the last assessment in the areas of observations, laboratory measurements, and modeling. These new results reaffirm the key role of anthropogenic halocarbons as the cause of ozone loss in polar regions and increase confidence in the processes associated with this loss: the formation of a polar vortex in high-latitude winter, the growth of aerosol surfaces at low temperatures characteristic of the vortex, the conversion of inactive chlorine to active forms on these surfaces, the subsequent chlorine-catalyzed loss of ozone, the return of chlorine to inactive forms in the polar regions in spring, and the breakup of the vortex and its dispersal to lower latitudes.

Ozone

- Results of observational and modeling studies since the last assessment reaffirm the role of anthropogenic halocarbon species in Antarctic ozone depletion. Satellite observations show a strong spatial and temporal correlation of chlorine monoxide (ClO) abundances with ozone depletion in the Antarctic vortex. Photochemical model calculations of ozone depletion are consistent with observed losses in the Antarctic.
- Chlorine- and bromine-catalyzed ozone loss has been confirmed in the Arctic winter. Consistent with expectations, these losses are smaller than those observed over Antarctica. Photochemical model calculations constrained with *in situ* and satellite observations yield results consistent with the observed ozone loss.
- Interannual variability in the photochemical and dynamical conditions of the vortices continues to limit reliable predictions of future ozone changes in polar regions, particularly in the Northern Hemisphere.

Chlorine Species

- Satellite measurements show that elevated ClO concentrations cover most of both polar vortex regions during much of the winter. This is consistent with the picture that virtually all available chlorine becomes fully activated in both winter vortices through heterogeneous reactions that occur on aerosol particles formed at low temperatures.
- *In situ* and remote measurements show that hydrochloric acid (HCl) and chlorine nitrate ($ClONO_2$) concentrations are markedly reduced in the vicinity of the elevated ClO concentrations. This anticorrelation is quantitatively consistent with the picture that HCl and $ClONO_2$ are converted to reactive chlorine. Chlorine in the stratosphere originates largely from anthropogenic halocarbons.

Aerosols

- Laboratory studies reaffirm that surface reactions on aerosol particles efficiently produce active chlorine from inactive forms. The rate of the principal reaction of HCl with $ClONO_2$ is a strong function of temperature and relative humidity, and depends to a lesser extent on bulk aerosol composition.
- Sulfate aerosol from the Mt. Pinatubo eruption reached high latitudes in the stratosphere, enhancing reactions involving aerosol particles in and near the polar vortices. This led to chlorine activation over larger regions in the high latitude stratosphere, especially near the vortex boundaries, and extended the spatial extent of halogen-related ozone loss.
- The formation and reactivity of aerosol particles within the vortex can be simulated, in part, by microphysical models. Two- and three-dimensional photochemical transport models confirm observations that chlorine can be activated efficiently throughout the entire vortex within days.
- Aerosol particles in the polar stratosphere are known ternary condensates of nitric acid (HNO_3), sulfuric acid (H_2SO_4), and water (H_2O). Important progress has been made in the characterization of these condensates in theoretical and laboratory studies.
- Satellite measurements confirm that the sequestering and removal of HNO_3 by aerosol particles is a predominant feature of the Antarctic vortex for much of the winter, whereas removal in the Arctic is generally less intense and more localized.
- Despite extensive observational evidence for dehydration and denitrification, the underlying microphysical mechanisms and necessary atmospheric conditions that control particle formation and sedimentation have not been adequately described. This is an important limitation for reliably predicting ozone loss in polar regions, particularly in the Northern Hemisphere.

Vortex

- New satellite observations of long-lived tracers and modeling studies confirm that air within the center of the polar winter vortices is substantially isolated from extravortical air, especially in the Antarctic.

- Nearly all observational and modeling studies are consistent with a time scale of three to four months to replace a substantial fraction of inner Antarctic vortex air.
- Models show that most mass transport out of the vortex in the lower stratosphere occurs below about 16 km altitude.
- Erosion by planetary and synoptic wave activity transports air from the vortex edge region to lower latitudes. Data and model studies provide conflicting interpretations of the magnitude of this transport and its effect on lower latitudes. There is little evidence of significant lateral mixing into the vortex except during strong wave events in the Arctic.
- Observed correlations of nitrous oxide abundances with those of inactive chlorine species, reactive nitrogen, and ozone over broad regions at high latitudes in the lower stratosphere have proved useful for diagnosing ozone destruction throughout the vortex.

CHAPTER 4: TROPICAL AND MID-LATITUDE OZONE

Since the last Assessment, much new information has been obtained about the photochemical and dynamical processes that influence ozone concentrations at middle latitudes. Measurements in the lower stratosphere have significantly increased our confidence in the basic gas phase and heterogeneous processes affecting ozone at middle latitudes, although some discrepancies still exist. Laboratory studies have provided data that have led to an improved quantification of the photochemical processes that affect ozone at middle latitudes. Understanding of the dynamical factors influencing middle latitudes has improved, although significant uncertainties remain. The relative contributions of these different processes to the ozone trends observed middle latitude are still poorly understood and important uncertainties are still outstanding.

The major new findings are:

Photochemical Processes

- Observations, coupled with photochemical model calculations, have established with little doubt the role of the heterogeneous hydrolysis of N_2O_5 on the sulfate aerosol layer. However, there are instances where discrepancies still arise, and it is unclear whether these reflect deficiencies in modeling known chemistry (e.g., imperfect knowledge of aerosol surface areas, photolysis rates, etc.) or, more profoundly, missing chemical processes.
- Measurements of radical species in the low stratosphere have provided direct confirmation that *in situ* photochemical ozone loss in the lower stratosphere at mid-latitudes is dominated by HO_x and (man-made) halogen chemistry, and not by (largely natural) NO_x chemistry. Nevertheless, NO_x chemistry exerts an important control on the effectiveness of the halogen loss cycles. Current photochemical models can reproduce observed radical concentration changes and coupling between different chemical families, provided that heterogeneous reactions are incorporated and that the source gases are suitably constrained by observations.
- Satellite and *in situ* measurements of chlorine monoxide (ClO) concentrations in the low stratosphere at middle latitudes in both hemispheres show the existence of a seasonal cycle with maximum ClO during winter months. This variation appears to be broadly consistent with changes in NO_x due to *in situ* heterogeneous processes but does not appear consistent with the timing of springtime vortex dilution or wintertime flow through the vortex.

- There is evidence that the hydrolysis of chlorine nitrate ($ClONO_2$) on sulfate aerosols can occur at low temperatures and may be important in middle latitudes under high aerosol loading conditions.
- There are unresolved discrepancies between models and observations regarding the partitioning between reservoir and reactive species, notably the ratio of ClO_x to HCl. Even when constrained by observed source gas fields and radical species, photochemical models in the low stratosphere significantly overestimate observed HCl amounts. In the upper stratosphere models overestimate the ClO/HCl ratio.

Laboratory Studies

- Recent studies have confirmed that N_2O_5 hydrolysis on sulfate aerosol surfaces is fast and occurs readily under most stratospheric conditions, while reactions that lead directly to chlorine activation depend strongly on atmospheric temperature and humidity.
- The rate of the reaction of BrO with HO_2 has been revised upwards by a factor of 6, implying a much larger bromine-catalyzed ozone loss in the low stratosphere.
- Quenching rates for vibrationally excited O_2 appear to be faster than previously thought, reducing the likely importance of the photolysis of vibrationally excited O_2 as a source of ozone in the upper stratosphere. The discrepancy between observed and modeled ozone in this region still persists.

Dynamical Processes

- The transport of air from polar regions has the potential to influence ozone concentrations at middle latitudes. While there are uncertainties about the relative contributions of transport and *in situ* chemistry for mid-latitude ozone loss, both processes directly involve ozone destruction by bromine- and chlorine-catalyzed reactions.
- Observations and models indicate that, above about 16 km in winter, air at mid-latitudes is mixed relatively efficiently and that influx of air from the tropics and from the interior of the polar vortex is weak. However, the importance of the erosion of air from the edge of the polar vortex relative to *in situ* chemical effects for mid-latitude ozone loss is poorly known.
- Below 16 km, air is more readily transported between polar regions and mid-latitudes. The influence of this transport on mid-latitude ozone loss has not been quantified.

Eruption of the Mt. Pinatubo Volcano

- The eruption of Mt. Pinatubo in 1991 led to a massive increase in sulfate aerosol in the lower stratosphere. There is compelling evidence that this led to significant, but temporary, changes in the partitioning of NO_x, reactive halogen compounds, and abundances of HO_x in the low and mid-stratosphere at middle latitudes in such a way as to accelerate photochemical ozone loss. However, there is also evidence that circulation changes associated with heating on Mt. Pinatubo aerosols led to significant changes in the distribution of ozone in the tropics and middle latitudes. Changes in photolysis rates arising directly from the presence of volcanic aerosols are also thought to have affected ozone amounts.

CHAPTER 5: TROPOSPHERIC OZONE

Although representing only 10 percent of the total ozone column, tropospheric ozone is important because it can influence climate, as it is a greenhouse gas itself, and because its photolysis by UV radiation in the presence of water vapor is the primary source for hydroxyl radicals (OH). Hydroxyl radicals are responsible for the oxidative removal of many trace gases, such as methane (CH_4), hydrofluorocarbons (HFCs), and hydrochlorofluorocarbons (HCFCs), that influence climate and/or are important for the stratospheric ozone layer.

Tropospheric ozone arises from two processes: Downward flux from the stratosphere; and *in situ* photochemical production from the oxidation of hydrocarbons and carbon monoxide (CO) in the presence of NO_x ($NO + NO_2$). Ozone is removed from the troposphere by *in situ* chemistry and by uptake at the Earth's surface. The role of photochemistry in the local ozone balance depends strongly on the concentration of NO_x. Human impact on tropospheric ozone and hydroxyl occurs through the emission of precursors, *e.g.*, NO_x, CO, and hydrocarbons. In the case of free tropospheric ozone, this is brought about by the export of both ozone and its precursors, in particular NO_x, from source regions.

While substantial uncertainties remain in assessing the global budget of tropospheric ozone, recent studies have led to significant advances in understanding the local balance of ozone in some regions of the atmosphere.

- Recent measurements of the NO_y/O_3 ratio have basically confirmed earlier estimates of the flux of ozone from the stratosphere to be in the range of 240-820 $Tg(O_3)/yr$, which is in reasonable agreement with results from general circulation models (GCMs).
- The observed correlation between ozone and alkyl nitrates suggests a natural ozone concentration of 20 to 30 ppb in the upper planetary boundary layer (at about 1 km altitude), which agrees well with the estimate from the few reliable historic data (c.f. Figure 1-16, Chapter 1).
- Measurements of the gross ozone production rate yielded values as high as several tens of ppb per hour in the polluted troposphere over populated regions, in good agreement with theoretical predictions. Likewise, the efficiency of NO_x in ozone formation in moderately polluted air masses was found to be in reasonable agreement with theory.
- Direct measurements of hydroxyl and peroxy radicals have become available. While they do not serve to establish a global climatology of OH, they do provide a test of our understanding of the fast photochemistry. To date, theoretical predictions of OH concentrations (from measured trace gas concentrations and photolysis rates) tend to be higher than the measurements by up to a factor of two.
- Measurements of peroxy radical concentrations in the remote free troposphere are in reasonable agreement with theory, however, significant misunderstanding exists with regard to the partitioning of odd nitrogen and the budget of formaldehyde.
- Measurements have shown that export of ozone produced from anthropogenic precursors over North America is a significant source for the North Atlantic region during summer. It has also been shown that biomass burning is a significant source for ozone in the tropics during the dry season. These findings show the influence of human activities on the global ozone balance.

- Photochemical net ozone destruction in the remote atmosphere has been identified in several experiments. It is likely to occur over large parts of the troposphere with rates of up to several ppb per day. Consequently, an increase in UV-B radiation (e.g., from stratospheric ozone loss) is expected to decrease tropospheric ozone in the remote atmosphere but in some cases will increase production of ozone in and transport from the more polluted regions. The integrated effect on hydroxyl concentrations and climate is uncertain.

Uncertainties in the global tropospheric ozone budget, particularly in the free troposphere, are mainly associated with uncertainties in the global distribution of ozone itself and its photochemical precursors, especially CO and NO_x. These distributions are strongly affected by dynamics, by the magnitude and spatial/temporal distribution of sources, particularly those for NO_x to the middle and upper troposphere from the stratosphere, lightning, aircraft, and convective systems, and by the partitioning and removal of NO_y constituents. The role of heterogeneous processes including multiphase chemistry in the troposphere is not well characterized and the catalytic efficiency of NO_x in catalyzing ozone formation in the free troposphere has not been confirmed by measurements.

CHAPTER 6: MODEL SIMULATIONS OF STRATOSPHERIC OZONE

- Multi-dimensional models are designed to provide simulations of the large-scale transport in the stratosphere. This transport rate is combined with the local chemical production and removal rates of ozone to determine the distribution of ozone as a function of longitude, latitude, height, and season.
- There is strong observational evidence that heterogeneous chemistry (hydrolysis of N_2O_5 and $ClONO_2$) is operating on surfaces of the aerosol particles in the stratospheric sulfate layer. There is a general agreement on how this should be represented in the models. Models that include these reactions produce calculated ozone decreases (between 1980 and 1990) that are larger and in better agreement with the observed trend than those produced by models that include only gas-phase reactions. All model simulations reported here include these two reactions.
- Both three-dimensional and two-dimensional models have been used in simulating polar stratospheric cloud (PSC) chemistry in the vortex and how the equatorward transport of chemically perturbed polar air may affect ozone at midlatitudes. Our lack of understanding of the detailed mechanisms for denitrification, dehydration, and transport processes reduces our confidence in these model predictions.
- No multi-year simulation has been performed to date using three-dimensional models. Two-dimensional (latitude-altitude) models remain the primary tools for extensive diagnostic studies and multi-year simulations.

How well do models simulate the distributions and trends of ozone in the stratosphere?

Upper Stratosphere

- The model-simulated ozone concentration in the upper stratosphere is typically 20% smaller than the observed values, a problem that has been identified previously. This suggests that there is a problem with our understanding of the photochemistry in that region.
- The model-calculated ozone trends above 25 km due to emission of halocarbons between 1980 and 1990 are in reasonable agreement with the trends (both in the altitude profile and latitudinal variation) derived from the satellite measurements. Most of the model results did not consider radiative feedback and temperature trends that are likely to reduce the predicted ozone decreases by about a factor of 0.8.

Lower Stratosphere

- The models underestimate the amount of ozone in the lower stratosphere at high latitudes during winter and spring. This, coupled with the model-calculated behaviors of other trace gases, indicates that the models do not have a good representation of the transport processes in those seasons.
- The partitioning of the radical species in the lower stratosphere is influenced to a large extent by the hydrolysis rates of N_2O_5 and $ClONO_2$. This, in turn, affects the calculated ozone response in the lower stratosphere to increases in chlorine and bromine. The trend in the polar region is also affected by PSC chemistry in the vortex as well as heterogeneous conversion of HCl on sulfate particles at cold temperatures.
- Comparison with the local trend derived from observations indicates that models that include only hydrolysis of N_2O_5 and $ClONO_2$ on sulfate particles underestimate the trend between 15 and 20 km at all latitudes. Including PSC processing and the heterogeneous conversion of hydrochloric acid (HCl) on cold sulfate aerosol in model simulations gives larger trends at high latitudes.

Column Abundance

- The model-simulated ozone columns in the tropics are within 10% of the observed values. However, some models underestimate the spring maximum in the Northern Hemisphere by as much as 30%.
- The models calculate a trend in the tropics of about -1% per decade in the column abundance of ozone due to emissions of halocarbons between 1980 and 1990. This is consistent with the trend derived from the Dobson stations, the Solar Backscatter Ultraviolet (SBUV) instrument, and the Total Ozone Mapping Spectrometer (TOMS). The model-calculated trend in the tropics is largely a result of the calculated ozone decrease above 25 km.

- The decreases in column ozone at high latitudes calculated by models that include hydrolysis of N_2O_5 and $ClONO_2$ as the only heterogeneous reactions are between 2% to 3% per decade. This is smaller than the observed negative trends of 4% to 8% per decade at the northern high latitudes, and 8% to 14% at southern high latitudes outside the vortex.
- Models with PSC chemistry calculate a trend at high latitudes comparable to observation. However, the trend at mid-latitudes is still small compared to the observed decrease of 4%-6% during winter and spring (Northern Hemisphere) and winter and summer (Southern Hemisphere).
- A larger trend can be obtained at mid-latitudes by including the effects from export of chemically perturbed air from the polar region, by adjusting the transport, or by invoking additional chemical ozone removal cycles. The importance of the processes has not been resolved because of the lack of laboratory and field data.
- The increase in aerosol loading due to the eruption of Mt. Pinatubo was predicted to perturb the lower stratosphere. An idealized simulation was designed to isolate the effect of the photochemical response to a uniform thirty-fold increase in aerosol loading starting in June that decays with a time constant of 1 year. The model-calculated decreases range from 2% to 8% around 50°N in the spring after the prescribed increase, with the calculated decrease diminishing to zero over a five-year period.

Model Predictions of Future Trends

- Using an emission scenario that is designed to represent global compliance with the international agreements, the calculated chlorine loading in the stratosphere reaches its maximum value about 3 to 5 years after the prescribed tropospheric organic chlorine concentration achieves its maximum value. The maximum calculated chlorine and bromine concentrations and the lowest ozone values occur within 2 years of each other in this scenario.
- Comparison of the model results indicates that although there are significant differences among the model-calculated local photochemical rates and transport rates, the rates from each individual model combine to produce reasonable present-day ozone distributions and the 1980 to 1990 ozone trend. However, as the atmosphere is perturbed farther away from its present state (e.g., large increase in aerosol loading, changes due to long-term trends of N_2O, CH_4 and halocarbons), the model-predicted responses differ by larger amounts. Current efforts aimed at direct validation of the transport process and photochemical process will help to resolve the differences and bolster our confidence in the model predictions.

CHAPTER 7: MODEL SIMULATIONS OF GLOBAL TROPOSPHERIC OZONE

Simulations of chemical tracers and comparison with observations indicate that global three-dimensional (3-D) models are able to describe gross features of atmospheric transport, such as boundary layer ventilation and long-range transport from continents to oceans. The broad distributions of the tropospheric ozone, such as altitudinal and seasonal variation, are captured to within about a factor 2. Important inaccuracies still remain: stratospheric/tropospheric exchange, natural emissions of precursors (e.g., NO_x from lightning), reactions in aerosols and clouds, and representation of processes not resolved at the scale of models.

Three-dimensional simulations of O_3 over polluted continents have shown some success in reproducing observed distributions of ozone, NO_x, NO_y, and hydrocarbons under conditions where emissions and meteorology are well characterized.

Models and analyses of observations show evidence for a large anthropogenic contribution to tropospheric ozone in the Northern Hemisphere (NH). A few global model studies report that tropospheric ozone has increased by more than 50% since pre-industrial times over large regions of the NH lower and middle troposphere.

The global mean hydroxyl radical (OH) concentrations predicted by a variety of 2-D and 3-D models are within a factor 1.3 of the values that have been derived from budget studies of methyl chloroform (CH_3CCl_3) and hydrochlorofluorocarbons (HCFCs), and are also consistent with analysis of ^{14}CO.

Two model intercomparison exercises have been conducted to test the ability of models to simulate a) the transport of short-lived tracers and b) basic features of O_3 photochemistry. More than twenty models participated. A high degree of consistency was found in the global transport of a short-lived tracer within the 3-D chemistry transport models (CTMs). General agreement was also found in the computation of photochemical rates affecting tropospheric O_3. These are the first extensive intercomparisons of global tropospheric models.

2-D tropospheric chemistry models capture the coarse features of the ozone distribution and are useful for some analyses. Quantitative assessments based on these models will remain highly uncertain. The model intercomparison cited above showed that 2-D models cannot transport short-lived species in the same manner or magnitude as 3-D models.

A set of five 2-D and 3-D models predicted the O_3 change expected for a 20% increase in methane (CH_4) concentration. All models predicted small tropospheric O_3 increases, ranging from 0.5 to 2.5 ppb in the tropics and the mid-latitude northern summer. The large range in the results demonstrates the large uncertainty in quantitative assessment. All models predicted an increase in the effective CH_4 lifetime.

These simulations and a theoretical analysis of the tropospheric chemical system coupling CH_4, CO, and OH have shown that CH_4 perturbations decay with a lengthened time scale, about 13.6 (11.3 to 16.0) yr, as compared with the lifetime derived from total abundance and losses, about 9.4 yr. This longer residence time describes the decay of any reasonably sized methane pulse, including all associated perturbations to tropospheric O_3 and stratospheric H_2O. It also increases our estimate of the greenhouse effectiveness of CH_4 emissions by a factor 1.45 as compared with previous assessments.

CHAPTER 8: RADIATIVE FORCING AND TEMPERATURE TRENDS

Radiative Forcing and Climatic Impact of Ozone Change

- Recent one-dimensional studies support earlier conclusions that between 1980 and 1990 the observed decrease in stratospheric ozone has caused a negative global-mean radiative forcing (i.e., it acts to cool the climate) that is about -0.1 Wm^{-2}; this can be compared to the direct radiative forcing due to changes in CO_2, CH_4, N_2O, and the chlorofluorocarbons (the "well-mixed" gases) of about 0.45 Wm^{-2} over the same period. An accurate assessment of the

potential climatic effect of changes in stratospheric ozone is limited by the lack of detailed information on the ozone change, especially in the vicinity of the tropopause. A limited sensitivity study using different assumptions about the vertical profile of ozone loss indicates that, for the same change in total column ozone, the ozone forcing could conceivably be up to a factor of two less negative.

- Model simulations and deductions from limited observations of the increase in tropospheric ozone since pre-industrial times suggest a positive global-mean forcing that may be around 0.5 Wm^{-2}; this can be compared to the direct radiative forcing due to changes in well-mixed gases of about 2.4 Wm^{-2} over the same period. Particular difficulties are the verification of the geographical extent of the tropospheric ozone increases and the problems in accurately specifying the vertical profile of the change.
- On the basis of these estimates, the net global-mean radiative forcing due to ozone changes is likely to have been positive since pre-industrial times. However, Chapter 1 indicates that tropospheric ozone has changed little since 1980 and so, since then, the stratospheric ozone change is likely to have dominated, giving a negative global-mean forcing due to ozone changes.
- An intercomparison of radiation codes used in assessments of the radiative forcing due to ozone changes has shown that, in general, differences between these codes can be explained; the intercomparison highlights the detail with which solar and thermal infrared processes must be represented.
- The only general circulation model (GCM) experiment to investigate the climatic impact of observed lower stratospheric ozone loss between 1970 and 1990 indicates the expected surface cooling in response to the negative radiative forcing.
- Other GCM simulations raise important, but as yet unresolved, issues about the way in which the global mean of a spatially very inhomogeneous radiative forcing, such as that due to ozone change, can be directly compared to the global-mean forcing due to, for example, changes in well-mixed greenhouse gases.
- The previous assessment noted that the negative radiative forcing due to stratospheric ozone loss in the 1980s is of a similar size as, but the opposite sign to, the positive direct radiative forcing due to halocarbons over the same period. Attempts have been made to partition the indirect negative forcing due to ozone loss amongst individual halocarbons. They have emphasized that bromocarbons are, on a per molecule basis, much more efficient at destroying ozone than chlorofluorocarbons (CFCs). One evaluation attributes about 50% of the 1980-1990 negative forcing to the CFCs; since the CFCs dominate the direct forcing, their net effect is reduced by about 50% due to the ozone loss. Carbon tetrachloride and methyl chloroform each contribute about 20%, while bromocarbons contribute about 10% to the indirect forcing; these species contribute relatively little to the direct forcing so their net effect is likely to be negative.

Lower Stratospheric Temperature Trends

- The temperature of the lower stratosphere showed a marked rise, of about 1 deg C in the global mean, due to the radiative effects of increases in stratospheric aerosol loading following the eruption of Mt. Pinatubo in June 1991. The maximum warming occurred in the six months following the eruption; temperatures have now returned to near pre-eruption levels. This warming has been successfully simulated by GCMs.
- Data from radiosondes over the past three decades and satellite observations since the late 1970s continue to support the existence of a long-term global-mean cooling of the lower stratosphere of about 0.25 to 0.4 deg C/decade; there is some indication of an acceleration in this cooling during the 1980s, but the presence of large temperature perturbations induced by volcanic aerosols makes trend analysis difficult.
- Model calculations indicate that ozone depletion is likely to have been the dominant contributor to the temperature trend in the lower stratosphere since 1980 and is much more important than the contribution of well-mixed greenhouse gases. In addition, observed temperature trends since 1979 are found to be significantly negative at the same latitudes and times of year as significant decreases in column ozone, with the exception of the southern mid-latitudes in mid-winter. However, there are other potential causes of lower stratospheric temperature change (such as changes in stratospheric water vapor or cirrus clouds) whose contributions are difficult to quantify.

Radiative Properties of Halocarbon Substitutes

- More laboratory measurements of the infrared absorption cross-sections of actual and proposed substitutes to chlorofluorocarbons have become available, including molecules not hitherto reported in assessments. These cross-sections have been included in radiative transfer models to provide estimates of the radiative forcing per molecule. The radiative forcing estimates are subjectively estimated to be accurate to within 25%, but not all of the studies have yet been reported in adequate detail in the open literature; this hinders a detailed understanding of differences in existing estimates.

CHAPTER 9: SURFACE ULTRAVIOLET RADIATION

- There is overwhelming experimental evidence that, all other things being equal, decreases in atmospheric ozone result in UV-B increases at the Earth's surface, in quantitative agreement with predictions by radiative transfer models.
- Large UV-B increases have been observed in association with the ozone "hole" at high southern latitudes. Biologically damaging radiation at the South Pole exceeded that in the Arctic by more than a factor of two, for the same solar zenith angle. At Palmer Station, Antarctica (64.5°S), erythemal and DNA-damaging radiation sometimes exceeded summer maxima at San Diego (32°N). These measured differences agree well with model calculations.

- Large increases in UV-B were measured, despite the natural variability in cloudiness, at northern middle and high latitudes in 1992/93 compared with previous years. These are the first reported examples of persistent increases associated with anomalous ozone reductions over densely populated regions.
- Clear-sky UV measurements at midlatitude locations in the Southern Hemisphere are significantly larger than at a mid-latitude site in the Northern Hemisphere, in agreement with the expected differences due to ozone column and Sun-Earth separation.
- The increases in UV resulting from ozone reductions measured by satellite from 1979 to early 1994 have been calculated, assuming other factors such as pollution and cloudiness did not change systematically over this period. The calculated increases are largest at short wavelengths and at high latitudes. Poleward of 45°, the increases are significantly greater in the Southern Hemisphere. At 45° (N and S), the calculated increase at 310 nm was approximately 8 to 10 percent over this 15-year period, but there was considerable year-to-year variability.
- Tropospheric ozone and aerosols can reduce global UV-B irradiances appreciably. At some locations, tropospheric pollution may have increased since pre-industrial times, leading to some decreases in surface UV radiation. However, recent trends in tropospheric pollution probably had only minor effects on UV trends relative to the effect of stratospheric ozone reductions.
- Only a few studies have monitored UV-B over time scales of decades, and these have yielded conflicting results on the magnitude and even sign of the trends. Some studies may have been affected by problems with instrument stability and calibration, and local pollution trends. Recently published data from unpolluted locations appear to show the expected increases due to ozone depletion. The baseline UV irradiances present at mid and high latitudes before ozone depletion began are not known.
- Significant improvements have been made in UV instrumentation and its calibration. Intercomparisons between spectro-radiometers show, however, that it is still difficult to achieve absolute calibration accuracies better than ±5 percent in the UV-B region. Therefore, the detection of future trends will require careful measurements at short wavelengths that are more sensitive to changes in ozone.
- Cloud variability causes large temporal changes in UV. Although recent advances have been made, our ability to realistically model cloud effects is still limited.
- Scattering by stratospheric aerosols from the Mt. Pinatubo volcanic eruption did not alter total UV irradiances appreciably, but did increase the ratio of diffuse to direct radiation.

CHAPTER 10: METHYL BROMIDE

- Four potentially major sources for atmospheric methyl bromide (CH_3Br) have been identified: the ocean, which is a natural source, and three others that are almost entirely anthropogenic; these are agricultural usage, which has been reaffirmed, biomass burning, which is newly recognized, and the exhaust of automobiles using leaded gasoline.

- The estimated uncertainty range for these sources is large, with oceans ranging from 60 to 160 ktonnes/yr, agriculture from 20 to 60 ktonnes/yr, biomass burning from 10 to 50 ktonnes/yr, and automobile exhaust from 0.5 to 22 ktonnes/yr. In the latter case, the range results from two conflicting assessments, which yield 0.5 to 1.5 ktonnes/yr and 9 to 22 ktonnes/yr, respectively.
- There are also two minor anthropogenic sources, structural fumigation (4 ktonnes/yr) and industrial emissions (2 ktonnes/yr), each of which are well quantified.
- Measurements of CH_3Br yield a global average ground-level atmospheric mixing ratio of approximately 11 pptv. These measurements also have confirmed that the concentration in the Northern Hemisphere is higher by about 30% than the concentration in the Southern Hemisphere (interhemispheric ratio of 1.3). Such a ratio requires that the value of sources minus sinks in the Northern Hemisphere exceeds the same term in the Southern Hemisphere.
- There is no clear long-term change in the concentration of CH_3Br during the time period of the systematic continued measurements (1978 to 1992). One possible explanation is that CH_3Br from automobiles may have declined while, at the same time, emissions from agricultural use may have increased, leading to relatively constant anthropogenic emissions over the last decade.
- The magnitude of the atmospheric sink of CH_3Br due to gas-phase chemistry is well known and leads to a lifetime of 2 ± 0.5 yr. The recently postulated oceanic sink leads to a calculated atmospheric lifetime due to oceanic hydrolysis of 3.7 yr, but there are large uncertainties (1.3 to 14 yr). Thus the overall atmospheric lifetime due to both of these processes is 1.3 yr with a range of 0.8 to 1.7 yr.
- Recognizing the quoted uncertainties in the size of the individual sources of CH_3Br, the most likely estimate is that about 40% of the source is anthropogenic. The major uncertainty in this number is the size of the ocean source. Based on the present atmospheric mixing ratio and the current source estimate, a lifetime of less than 0.6 yr would require identification of new major sources and sinks.
- The chemistry of ozone destruction by bromine in the stratosphere is now better understood. A high rate coefficient for the HO_2 + BrO reaction is confirmed and there is no evidence that it produces HBr. A conservative upper limit of 2% can be placed on the reaction channel yielding HBr. Stratospheric measurements confirm that the concentration of HBr is very low (less than 1 pptv) and that it is not a significant bromine reservoir.
- The combined efficiency of the bromine removal cycles for ozone (HO_2 + BrO and ClO + BrO) is likely to be about 50 times greater than the efficiency of known chlorine removal cycles on an atom-for-atom basis.
- The calculated Ozone Depletion Potential (ODP) for CH_3Br is currently estimated to be 0.6 based on an atmospheric lifetime of 1.3 years. The range of uncertainties in the parameters associated with the ODP calculation places a lower limit on the ODP of 0.3.

CHAPTER 11: SUBSONIC AND SUPERSONIC AIRCRAFT EMISSIONS

Extensive research and evaluations are underway to assess the atmospheric effects of the present and future subsonic aircraft fleet and of a projected fleet of supersonic transports. Assessment of aircraft effects on the atmosphere involves the following:

- measuring the characteristics of aircraft engine emissions;
- developing three-dimensional (3-D) inventories for emissions as a function of time;
- developing plume models to assess the transformations of the aircraft engine emissions to the point where they are governed by ambient atmospheric conditions;
- developing atmospheric models to assess aircraft influences on atmospheric composition and climate; and
- measuring atmospheric trace species and meteorology to test the understanding of photochemistry and transport as well as to test model behavior against that of the atmosphere.

Supersonic and subsonic aircraft fly in atmospheric regions that have quite different dynamical and chemical regimes. Subsonic aircraft fly in the upper troposphere and in the stratosphere near the tropopause, where stratospheric residence times due to exchange with the troposphere are measured in months. Proposed supersonic aircraft will fly in the stratosphere near 20 km, where stratospheric residence times due to exchange with the troposphere increase to years. In the upper troposphere, increases in NO_x typically lead to increases in ozone. In the stratosphere, ozone changes depend on the complex coupling among HO_x, NO_x, and halogen reactions.

- Emission inventories have been developed for the current subsonic and projected supersonic and subsonic aircraft fleets. These provide reasonable bases for inputs to models. Subsonic aircraft flying in the North Atlantic flight corridor emit 56% of their exhaust emissions into the upper troposphere and 44% into the lower stratosphere on an annual basis.
- Plume processing models contain complex chemistry, microphysics, and turbulence parameterizations. Only a few measurements exist to compare to plume processing model results.
- Estimates indicate that present subsonic aircraft operations may have increased NO_x concentrations at upper tropospheric altitudes in the North Atlantic flight corridor by about 10 to 100%, water vapor concentrations by about 0.1% or less, SO_x by about 10% or less, and soot by about 10% compared with the atmosphere in the absence of aircraft and assuming all aircraft are flying below the tropopause.
- Preliminary model results indicate that the current subsonic fleet produces upper tropospheric ozone increases as much as several percent, maximizing at the latitudes of the North Atlantic flight corridor.
- The results of these rather complex models depend critically on NO_x chemistry. Since there are large uncertainties in the present knowledge of the tropospheric NO_x budget (especially in the upper troposphere), little confidence should be put in these quantitative model results of subsonic aircraft effects on the atmosphere.

- Atmospheric effects of supersonic aircraft depend on the number of aircraft, the altitude of operation, the exhaust emissions, and the background chlorine and aerosol loading. Rough estimates of the impact of future supersonic operations (assuming 500 aircraft flying at Mach 2.4 in the stratosphere and emitting 15 grams of nitrogen oxides per kilogram of fuel) indicate an increase of the North Atlantic flight corridor concentrations of NO_x up to about 250%, water vapor up to about 40%, SO_x up to about 40%, H_2SO_4 up to about 200%, soot up to about 100%, and CO up to about 20%.
- One result of two-dimensional model calculations of the impact of such a projected fleet in a stratosphere with a chlorine loading of 3.7 ppbv (corresponding to the year 2015), implies additional annually averaged ozone column decreases of 0.3 to 1.8% for the Northern Hemisphere. Although NO_x aircraft emissions have the largest impact on ozone, the effects from H_2O emissions contribute to the calculated ozone change (about 20%).
- Net changes in the column ozone from supersonic aircraft modeling result from ozone mixing ratio enhancements in the upper troposphere and lower stratosphere and depletion at higher stratospheric altitudes.
- There are important uncertainties in supersonic assessments. In particular, these assessment models produce ozone changes that differ among each other, especially in the lower stratosphere below 25 km. When used to calculate ozone trends, these same models predict smaller changes than are observed in the stratosphere below 25 km between 1980 and 1990. Thus, these models may not be properly including mechanisms that are important in this crucial altitude range.
- Increases in ozone at altitudes near the tropopause, such as are thought to result from aircraft emissions, enhance the atmosphere's greenhouse effect. Research to evaluate the climate effects of supersonic and subsonic aircraft operations is just beginning, so reliable quantitative results are not yet available, but some initial estimates indicate that this effect is of the same order as that resulting from the aircraft CO_2 emissions.

CHAPTER 12: ATMOSPHERIC DEGRADATION OF HALOCARBON SUBSTITUTES

The substitutes for long-lived halocarbons have been selected on the basis of either their susceptibility to oxidation in the lower part of the atmosphere and minimization of their transport to the stratosphere, or by absence of chlorine or bromine from the molecules. It has been assumed that the atmospheric degradation of the substitutes leads to products that do not cause ozone loss. Further, it is assumed that the degradation products have no other deleterious environmental effects.

These assumptions are examined in this chapter by assessing three aspects of chlorofluorocarbon (CFC) and halon substitutes: the factors that control their atmospheric lifetimes, the processes by which they are degraded in the atmosphere, and the nature of their degradation products. The main findings are:

- If a substance containing Cl , Br, or I decomposes in the stratosphere, it will lead to ozone destruction. Use of hydrochlorofluorocarbons (HCFCs) and other CFC substitutes containing Cl, Br, or I, which have short tropospheric lifetimes, will reduce the input of ozone-destroying substances to the stratosphere, leading to reduced ozone loss.
- None of the proposed CFC substitutes that are degraded in the troposphere will lead to significant ozone loss in the stratosphere via their degradation products.
- It is known that atomic fluorine itself is not an efficient catalyst for ozone loss and it is concluded that the F-containing fragments from the substitutes (such as CF_3O_x) also do not destroy ozone.
- Trifluoroacetic acid, formed in the degradation of certain HCFCs and hydrofluorocarbons (HFCs), will partition into the aqueous environment where biological, rather than physico-chemical, removal processes may be effective.
- The amount of long-lived greenhouse gases formed in the atmospheric degradation of HCFCs and HFCs appears to be insignificant.
- Certain classes of compounds, some of which have already been released to the atmosphere, such as perfluorocarbons, have extremely long atmospheric lifetimes and large global warming potentials.

CHAPTER 13: OZONE DEPLETION POTENTIALS, GLOBAL WARMING POTENTIALS, AND FUTURE CHLORINE/BROMINE LOADING

Scientific indices representing the relative effects of different gases upon ozone depletion and climate forcing are presented. Several scenarios for future chlorine/bromine loading are described that are aimed at implementation of the Copenhagen Amendments of the Montreal Protocol and the consideration of possible further options. Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) are evaluated with improved models and input data, and their sensitivities to uncertainties are considered in greater detail than in previous assessments. Major new findings are as follows:

- *Peak levels of ozone-depleting compounds are expected at stratospheric altitudes in the late 1990s.* Because current emission estimates suggest that the tropospheric chlorine/bromine loading will peak in 1994, further reductions in emissions would not significantly affect the timing or magnitude of the peak stratospheric halogen loading expected later this decade (*i.e.*, about 3 to 5 years after the tropospheric peak).
- *Approaches to lowering stratospheric chlorine and bromine abundances are limited.* Further controls on ozone-depleting substances would be unlikely to change the timing or the magnitude of the peak stratospheric halocarbon abundances and hence peak ozone loss. However, there are four approaches that would steepen the initial fall from the peak halocarbon levels in the early decades of the next century:
  - If emissions of methyl bromide from agricultural, structural, and industrial activities were to be eliminated in the year 2001, then the integrated effective future chlorine loading above the 1980 level (which is related to the cumulative future loss of ozone) is predicted to be 13% less over the next 50 years relative to full compliance to the Amendments and Adjustments to the Protocol.

- If emissions of hydrochlorofluorocarbons (HCFCs) were to be totally eliminated by the year 2004, then the integrated effective future chlorine loading above the 1980 level is predicted to be 5% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.
- If halons presently contained in existing equipment were never released to the atmosphere, then the integrated effective future chlorine loading above the 1980 level is predicted to be 10% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.
- If chlorofluorocarbons (CFCs) presently contained in existing equipment were never released to the atmosphere, then the integrated effective future chlorine loading above the 1980 level is predicted to be 3% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.

- *Failure to adhere to the international agreements will delay recovery of the ozone layer.* If there were to be additional production of CFCs at, for example, 20% of 1992 levels for each year through 2002 and ramped to zero by 2005 (beyond that allowed for countries operating under Article 5 of the Montreal Protocol), then the integrated effective future chlorine loading above the 1980 level is predicted to be 9% more over the next 50 years relative to full compliance to the Amendments and Adjustments to the Protocol.
- *Production of CF_3 from dissociation of CFCs, HCFCs, and hydrofluorocarbons (HFCs) is highly unlikely to affect ozone.* ODPs of HFCs containing the CF_3 group (such as HFC-134a, HFC-23, and HFC-125) are highly likely to be less than 0.001, and the contribution of the CF_3 group to the ODPs of HCFCs (*e.g.*, from HCFC-123) and CFCs is believed to be negligible.
- *ODPs for several new compounds such as HCFC-225ca, HCFC-225cb, and CF_3I have been evaluated using both semi-empirical and modeling approaches,* and estimated to be 0.03 or less.
- *Both the direct and indirect components of the GWP of methane have been estimated using model calculations.* Methane's influence on the hydroxyl radical and the resulting effect on the methane response time lead to substantially longer response times for decay of emissions than OH removal alone, thereby increasing the GWP. In addition, indirect effects including production of tropospheric ozone and stratospheric water vapor were considered and are estimated to range from about 15 to 45% of the total GWP (direct plus indirect) for methane.
- *GWPs including indirect effects of ozone depletion have been estimated for a variety of halocarbons (CFCs, halons, HCFCs, etc.), clarifying the relative radiative roles of different classes of ozone-depleting compounds.* The net GWPs of halocarbons depend strongly upon the effectiveness of each compound for ozone destruction; the halons are highly likely to have negative net GWPs while those of the CFCs are likely to be positive over both 20- and 100-year time horizons.
- *GWPs are not very sensitive to likely future changes in CO_2 abundances or major climate variables.* Increasing CO_2 abundances (from about 360 ppmv currently to 650 ppmv by the end of the 22nd century) could produce 20% larger GWPs for time horizons of the order of centuries. Future changes in clouds and water vapor are unlikely to significantly affect GWPs for most species.

- *GWPs for 16 new chemical species have been calculated, bringing the number now available to 38.* The new species are largely HFCs, which are being manufactured as substitutes for the CFCs, and the very long-lived fully fluorinated compounds, SF_6 and the perfluorocarbons.

SECTION C

1995 SCIENTIFIC ASSESSMENT OF THE ATMOSPHERIC EFFECTS OF STRATOSPHERIC AIRCRAFT

INTRODUCTION

The High-Speed Civil Transport (HSCT) is a proposed aircraft that would dramatically shorten inter-continental commercial flights. For example, transit times from Los Angeles to Tokyo would be short-ened from over 10 hours to less than 4 1/2 and flights from Los Angeles to Sydney from 14 hours to 7 1/2 hours, including a refueling stop. Such an aircraft might fly at Mach 2.4 (1600 mph) at an altitude of 20 km (65,000 ft), well into the stratosphere where most atmospheric ozone resides.

The 1995 Scientific Assessment of the Atmospheric Effects of Stratospheric Aircraft (NASA Reference Publication 1381) is a report commissioned by the NASA High Speed Research Program (HSRP), which has technology goals that, if achieved, would promise environmental compatibility and economic practicability for the HSCT fleet. When the program was conceived in 1989, this latest revival of interest in supersonic transport (SST) was greeted with healthy skepticism by those who well recalled the related atmospheric studies of the 1970s. For the technology of that era, it was predicted that nitrogen oxides (NO_x) from a fleet of SSTs would do significant damage to stratospheric ozone.

The current report represents scientific efforts directed at the atmospheric impacts of HSCTs that were made primarily under the auspices of the NASA Atmospheric Effects of Stratospheric Aircraft, Upper Atmosphere Research, and Atmospheric Chemistry and Analysis Programs. The assessment report seeks to describe research performed in the last few years and to help direct efforts that would further improve the ability to quantify and reduce uncertainties. For the purposes of this Congressional report, we present below the executive summary of the findings of the 1995 assessment report. The executive summary is organized into a series of questions that address the atmospheric environmental questions surrounding the proposed HSCT fleet.

EXECUTIVE SUMMARY

1. What are the concerns about high-speed civil transport operations in the stratosphere that motivate this assessment?

The operation of high-speed civil transport (HSCT) aircraft will introduce exhaust gases and particulates directly into the stratosphere. These exhaust components could alter stratospheric ozone and the Earth's climate.

- Important emissions from HSCTs include water vapor, carbon dioxide (CO_2), nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), nonmethane hydrocarbons (NMHCs), and soot. The atmospheric impact of these emissions depends on how they change the steady-state abundance over background atmospheric amounts and their role in

atmospheric photochemical, dynamical, and radiative processes. Atmospheric ozone change is possible because these HSCT emissions directly affect photochemical processes which control the ozone abundance. Climate change is also possible because these HSCT emissions are directly involved in the radiative balance of the atmosphere.

2. What processes are important in today's atmosphere and in a future atmosphere perturbed by HSCT emissions?

The amount of stratospheric ozone is determined by photochemical production and loss processes, and by the transport of air throughout the atmosphere. Photochemical loss of ozone is dominated by catalytic reactions involving NO_x, hydrogen oxides (HO_x), and halogen radicals (chlorine oxides (ClO_x) and bromine oxides (BrO_x)). Heterogeneous reactions which occur on or in stratospheric aerosol particles play an important role by reducing the ozone loss due to NO_x and increasing that due to HO_x and halogens. Atmospheric circulation determines the time spent by air in regions of photochemical loss and the distribution of exhaust gases emitted by a fleet of HSCTs.

- NO_x catalytically destroys stratospheric ozone but also inhibits ozone destruction by the HO_x and halogen radical catalytic cycles through the formation of more stable gases. The effect of adding NO_x to the atmosphere by HSCTs is sensitive to the balance of these two effects. In the stratosphere above ~26 km, NO_x catalysis is the most important ozone loss process; increased NO_x leads to increased local ozone loss. In the lower stratosphere, NO_x interference with the dominant HO_x and halogen catalysis of ozone destruction is more important. For increased NO_x (e.g., from HSCT exhaust), the sign and magnitude of the local chemical ozone change in the lower stratosphere depend on the background amounts of trace gases and aerosol surface area.
- Reactions on sulfate aerosols composed of sulfuric acid (H_2SO_4) and water (H_2O) play an important role in determining the abundance of NO_x. Because of these reactions, the concentration of NO_x depends on the variable input of volcanic SO_2 to the stratosphere. Observations show that the concentration of NO_x falls in response to increases in aerosol surface area. Because increases in sulfur, water vapor, and soot from HSCT emissions will change the surface area, composition, and number of particles in the lower stratosphere, the emissions indirectly influence ozone loss rates. In low-temperature regions near the poles, both liquid and frozen aerosols form that contain nitric acid (HNO_3) in addition to H_2O and H_2SO_4. Reactions on these aerosols enhance halogen-catalyzed loss of ozone and may sediment from the stratosphere, effectively reducing NO_x. The increased water vapor and H_2SO_4 from HSCT exhaust could increase the importance of such processes, especially if the stratosphere is cooled by climate change.
- Transport of air between mid-latitudes and the tropics is restricted, especially between 20 and 28 km. Transport of air from the primary flight corridors in mid-latitudes into the tropics results in a more rapid spread of HSCT exhaust from the lower to upper stratosphere, where the catalytic destruction of ozone by NO_x is more efficient.
- For a projected fleet of HSCT aircraft, climate can be affected by changes in the abundance of water vapor, soot, or sulfate in the stratosphere. Climate also can be affected by changes in cirrus cloud properties or by the radiative consequences of changes in ozone and its vertical distribution.

3. What has been learned about the character of engine emissions and the chemical and fluid-dynamic processing that occur in the aircraft wake?

In situ aircraft exhaust sampling experiments and modeling of engine processes and the dilution of exhaust gases into the atmosphere are used to define the important chemical and dynamical features of exhaust plumes in the stratosphere.

- Measurements of reactive nitrogen (NO_y) species, condensation nuclei (CN), and CO_2 were recently made in the exhaust of the Concorde supersonic aircraft and the NASA ER-2 subsonic aircraft while in flight. The emission indices (EIs) were calculated independently of plume dynamics because measurements of CO_2 provide a measure of fuel burned. The measured EI of NO_x, expressed as grams of equivalent nitrogen dioxide (NO_2) per kilogram of fuel burned, is in excellent agreement with earlier results deduced from altitude chamber measurements of exhaust from the Concorde engine as part of the Climatic Impact Assessment Program (CIAP). These results suggest that the methodology developed to calculate the EI of NO_x at cruise from altitude chamber data will be appropriate to evaluate new HSCT engines.
- Observations show that NO_x is the most abundant NO_y species in both supersonic and subsonic air craft plumes. The presence of only a small percentage of HNO_3 and nitrous acid (HONO) is in agreement with observations of HO_x in the plume and theoretical model calculations.
- The large number of detectable particles in the Concorde plume conflicts with the results of plume models that predict the formation of a large number of much smaller sulfate particles and a smaller fractional conversion of SO_x to condensed sulfate. These results indicate that current understanding of plume chemistry and particle formation processes is not complete. If new HSCT aircraft produce particles at a rate comparable to the Concorde, significant increases in particle number and surface area could occur in the lower stratosphere of the Northern Hemisphere. Including these increases in predictive models could change calculated ozone and climate impacts from an HSCT fleet.

4. What are the predicted atmospheric changes associated with HSCTs?

Five two-dimensional (2-D) photochemical models were used to calculate the impact of an HSCT fleet for a variety of cases including sensitivity tests for the EI of NO_x, cruise altitude, background atmospheric chlorine amount, and fleet size. Individual models were used to test sensitivity to a variety of effects not included in these basic predictive calculations.

- The range of model results is shown in Table ES-1. Conditions include a baseline fleet of 500 Mach 2.4 aircraft burning 8.2×10^{10} kg of fuel per year in an atmosphere with a background stratospheric aerosol amount equivalent to a relatively clean period between major volcanic eruptions. The models do not include the formation or reactivity of polar stratospheric cloud (PSC) particles. The calculated changes in ozone in Table ES-1 result from a decrease in the middle and upper stratosphere and an increase in the lower stratosphere and troposphere. The time required for photochemistry and transport to effect these ozone changes precludes large ozone changes near the assumed HSCT flight corridors.

Table ES-1. Calculated steady-state total column ozone change (%) in the Northern Hemisphere averaged over a year for several HSCT fleet scenarios.

Scenario				2-D model results
Mach number	Cl_y (ppbv)	EI_{NO_x} (g NO_2/kg fuel)	Number of aircraft	Ozone change (%)[a]
2.4	3	0	500	-0.3 to -0.1
2.4	3	5	500	-0.3 to +0.1
2.4	3	5	1000	-0.7 to +0.03
2.4	3	10	500	-0.5 to 0.0
2.4	3	15	500	-1.0 to -0.02
2.4	3	15	1000	-2.7 to -0.6
2.4 Cruise +1 km	3	5	500	-0.5 to +0.02
2.4 Cruise -2 km	3	5	500	-0.06 to +0.1
2.4	2[b]	5	500	-0.4 to +0.02

[a] Range of average values obtained from the five 2-D models used in this assessment.

[b]Expected in a 2050 atmosphere.

The EI_{NO_x} values in Table ES-1 reflect those expected for future HSCT combustors (5 g NO_2/kg fuel) and those closer to current engines (15 g NO_2/kg fuel).

- Laboratory observations continue to refine photolysis and reaction rate coefficients of importance to the lower stratosphere and to identify important reactions on surfaces of stratospheric aerosol particles. The formulation of the chemistry in the 2-D models is derived from the latest recommendation of a NASA panel that conducts a biennial review [DeMore *et al.*, 1994].
- Four of the five models used in the calculations were tested against two benchmarks, one for photolysis rates and one for chemistry. These indicate mostly minor differences, implying that the range in model results follows, at least in part, from differences in the 2-D representation of dynamics. The chemistry benchmark tested the model chemistry integrators against a photochemical steady-state model that has been used in detailed comparisons with atmospheric measurements of key radicals involved in the chemistry of stratospheric ozone.
- When the background aerosol surface area used in the models is increased by a factor of 4 (roughly equivalent to the median amount in the stratosphere over the last 2 decades), the calculated perturbation to total ozone is less negative by a few tenths of a percent. Variations in futurestratospheric aerosol levels, primarily due to the frequency of large volcanic eruptions, are a source of uncertainty in HSCT ozone impact predictions.

- Sulfur emitted by a fleet of HSCTs can increase the sulfate aerosol surface area throughout the lower stratosphere. Although the increase in surface area decreases the impact of NO_x emissions, it also in-creases ozone loss due to the existing chlorine and hydrogen radicals in the stratosphere. If the sulfur emitted by HSCTs immediately forms small particles in the plume, then the global increase in sulfate surface area is maximized.
- A model that included aerosol processes was used to calculate ozone changes when 100% of the sulfur (EI_{SO_2} = 0.4 g sulfur/kg fuel) from an HSCT fleet was emitted as small particles into a volcanically unperturbed stratosphere. The change in total column ozone from the injection of small particles depended in a complex way on EI_{NO_x} and background chlorine amount. For EI_{NO_x} = 5 g/kg fuel, the calculated ozone depletion increased when small particles were formed; the overall perturbation became as large or larger than that for the EI_{NO_x} = 15 g/kg fuel case. Inclusion of the reaction of $BrONO_2$ with water on aerosols increased the effect of the small particles.
- The model results for ozone change in the basic scenarios vary more widely when heterogeneous reactions on PSCs are included. This results from uncertainty in PSC microphysical processes and from ambiguity in how to best represent such processes in a 2-D model.
- A general circulation model (GCM) was used to calculate the global surface air temperature and stratospheric temperature responses to predicted changes in ozone and water vapor from a fleet of HSCTs with EI_{NO_x}= 15 g NO_2/kg fuel. Since the resulting changes in temperature are smaller than the climatic fluctuations in the model, they likely would not be detectable in the atmosphere.
- Climate effects due to sulfur and soot emissions, while likely to be small, have yet to be evaluated. Formation of persistent contrails from HSCTs is expected to be infrequent.

5. How consistent are atmospheric and laboratory measurements with the current representation of processes in the 2-D models used to predict the HSCT effects on ozone?

Atmospheric observations can provide tests of our understanding of the photochemical and transport processes responsible for controlling the distribution of ozone and the potential impact of HSCTs. Laboratory measurements define the formulation of chemistry in models. Subsets of this formulation are tested by comparing the model predictions against a sufficiently complete set of atmospheric observations. Although constraints on transport formulations in 2-D models are less direct, observations of the distribution of and the correlations between long-lived gases provide a test of these formulations. An extensive series of 2-D model tests, conducted in 1992 [Prather and Remsberg, 1993], led to improvements in the models and an understanding of the differences among them. Comparisons to observations made since that time are ongoing, as are further model improvements.

- Models reproduce the basic features of the ozone column and vertical profile. Consistent with observations, the models suggest that ozone concentrations should have decreased in the past decade. However, the predicted changes are smaller than those measured by a factor of 1.5 to 2, particularly in the lower stratosphere. Inclusion of a realistic representation of the temporal changes in stratospheric sulfate aerosol in a model improves the agreement with the

observed trends, but the predicted changes are still smaller than observed. These differences suggest that important uncertainties remain in the ozone changes calculated for an HSCT fleet.

- Model simulations reproduce some, but not all, of the basic features of the distribution of long-lived trace gases in the stratosphere. Since trace gases are the sources of the free radicals that catalyze ozone removal, model-measurement differences reflect inaccuracies in the model transport formulation and affect comparisons of reactive species calculations with measurements.

- Important regions for simulation of atmospheric transport are those with high spatial gradients in long-lived species such as N_2O, NO_y, or ozone. Examples are the regions in the stratosphere between the tropics and subtropics and at the edge of the polar vortices in winter. Aircraft and satellite observations have increased the level of understanding of the gradients and the barriers to transport that create them. In general, the 2-D models used to predict HSCT effects exhibit weak gradients, suggesting that they have too much mixing across these barriers.

- Observations of HO_x, NO_x, ClO_x, and BrO_x in the stratosphere allow direct evaluation of the photochemical destruction cycles of ozone. Above 25 km altitude, observations of HO_x and NO_x free radicals agree with photochemical models to within ~40% when the models are constrained by observed abundances of long-lived chemical species, temperature, aerosol surface area, and overhead ozone column. Observations of chlorine monoxide (ClO) at these altitudes are up to a factor of 2 lower than model predictions. Below 20 km, midday observations of HO_x, NO_x, ClO_x, and BrO_x also generally agree with similarly constrained models to within ~40%. However, HO_x observations exceed model calculations by more than a factor of 3 near sunrise and sunset, times when HO_x concentrations are small. Incorporation of the reaction of bromine nitrate ($BrONO_2$) with H_2O on sulfate aerosols reduces this discrepancy but increases the discrepancy in other species. Between about 20 and 25 km, observations of HO_x and ClO_x radicals are not available to provide a rigorous test of models.

- The observations and modeling of NO_x, HO_x, and ClO_x free radicals in the lower stratosphere agree in showing that the concentrations of HO_x and ClO_x depend on NO_x radicals. When the NO_x concentration is low, such as observed in the lower stratosphere of the Northern Hemisphere during the fall of 1992 and spring of 1993, the HO_x and ClO_x/BrO_x reactions dominate the local ozone loss rates. Thus, according to model calculations, when NO_x from HSCTs is added to these regions, reductions in HO_x and ClO_x/BrO_x abundances generally result in reductions in local ozone loss rates.

- Observations show that PSCs occur during the Antarctic winter and spring and Arctic winter. Heterogeneous reactions on these PSC surfaces activate large fractions of the available chlorine that can then destroy ozone in the presence of sunlight. Widespread ozone destruction does occur in the Antarctic because sedimenting PSC particles also denitrify the stratosphere and alter the buffering of ClO_x by NO_x. The proper inclusion of PSC processes in the 2-D predictive models would reduce an important uncertainty in the HSCT impact results.

6. What are the uncertainties in the atmospheric impacts of HSCT operations?

Several classes of uncertainty are associated with predictions of HSCT impacts made with 2-D models as shown in Table ES-1. Uncertainties in some model parameters can be readily quantified and evaluated directly with the models. Other sources of uncertainty have been identified but not yet quantified. Finally, uncertainty from the possibility of missing processes or major errors in understanding cannot be quantified, but only discussed in terms of the overall confidence in the assessment.

- The only quantified uncertainty in this assessment is that due to uncertainties in gas-phase reaction rate coefficients. These have been propagated through a model to give an estimated uncertainty of ~1% (1-σ) in the calculated ozone column perturbation in the Northern Hemisphere. Uncertainties in heterogeneous chemical reactions and photolysis rates will increase the overall chemical uncertainty. Constraining these results with atmospheric observations will reduce the uncertainty.
- A number of parametric sensitivity tests were performed for processes not included in the basic assessment scenarios. If the combined range of these tests is taken as an estimate of uncertainty, the overall uncertainty due to the processes not included in the basic scenarios is equal to or greater than the reaction-rate uncertainty.
- Uncertainties in microphysics include both the formation of numerous small particles in the HSCT exhaust plume and the possibility of increased denitrification in polar regions due to increases in condensible gases from the HSCT exhaust. Although the numerous small particles in the HSCT plume can indirectly affect ozone loss rates, the particle formation process is poorly understood and the uncertainties are large. Although the likelihood of a significant increase in Arctic denitrification and in polar ozone loss through chlorine and bromine chemistry is small, the implications of such processes for this assessment are large.
- Uncertainties in model transport remain important and difficult to quantify. Observations of seasonally varying and short- and long-lived tracers provide diagnoses of the degree of mixing and rates of transport between tropical and mid-latitude regions of the stratosphere, as well as providing information on residence times for stratospheric trace species.
- The impact of ozone and water vapor from HSCTs on climate was calculated to be within the climatic fluctuations of the model used. Thus, the expected perturbation and its uncertainty are difficult to quantify.
- The possibility of missing processes in the models creates an unquantifiable uncertainty in the HSCT assessment. However, the probability that important processes have been overlooked decreases as we continue to explore HSCT perturbations with models and continue to challenge these models with atmospheric measurements.

7. How can uncertainties in the predicted atmospheric effects of HSCTs be reduced?

Future efforts to reduce the overall assessment uncertainty are expected to focus on the major unquantified uncertainties and attempts to quantify them. The primary methodology for improving our predictive capability continues to involve testing model representations of the atmosphere through comparison with observational data. Substantial progress in that direction will be realized in the near term by systematic comparisons with recent data from the Upper Atmospheric Research Satellite (UARS), the Atmospheric Laboratory for Applications and

Science (ATLAS) on the Space Shuttle, and ER-2 aircraft, as well as a host of balloon platforms. Specific additional strategies for addressing the major uncertainties identified in this assessment are listed below in no specific order of priority:

- Extension of the observational database for long-lived tracers and radicals to include a number of seasonal cycles and undersampled regions of the atmosphere, notably the summer high latitudes and tropics.
- Systematic development of 3-D chemical-transport models for testing transport formulations and zonal-symmetry assumptions in 2-D predictive models.
- Inclusion of standardized descriptions of particle formation and evolution in 2-D predictive models and comparison with global aerosol distributions derived from existing satellite and aircraft data.
- Further characterization, through laboratory and atmospheric observations, of the composition and temporal evolution of aircraft exhaust aerosols in the wake/plume regime, and of the composition and microphysics of PSCs.

SECTION D

ATLAS END-OF-SERIES STATEMENT

The Atmospheric Laboratory for Applications and Science (ATLAS) series of Space Shuttle missions came to an end with the third flight of the ATLAS payload in November 1994. The ATLAS core payload consisted of six instruments designed to measure total solar irradiance, spectrally resolved solar ultraviolet irradiance, and the trace constituent composition of the Earth's stratosphere and mesosphere. Several other instruments flew together with the ATLAS core payload on each of the Shuttle flights, making for an integrated science payload governed by a single timeline for each flight.

The ATLAS series had originally been envisioned as a series of 10 Shuttle missions to fly over the course of an 11-year solar cycle. A combination of cost, schedule, and limited Shuttle manifest opportunities led to the termination of the ATLAS series after three missions. In spite of its early termination, the ATLAS flights have provided considerable information on solar output and the trace constituent distribution of the atmosphere. The ATLAS instruments also proved to be very effective in providing calibration information useful for comparison with that from instruments on free-flying spacecraft, notably the Upper Atmosphere Research Satellite (UARS) and the Solar Backscatter Ultraviolet (SBUV/2) instruments aboard the US National Oceanic and Atmospheric Administration (NOAA) operational meteorological satellites. The 57-degree inclination orbit used during the ATLAS missions allowed for obtaining data over a wide range of latitudes.

The instrument complement of the three ATLAS flights, including relevant co-manifested payloads, is included in Table 1. A summary of information on the three ATLAS flights is included in Table 2. With the exception of the MAS instrument, all of the core ATLAS payloads had flown previously; three (SOLCON, SOLSPEC, ACRIM) flew on Spacelab 1 (1983), while the SUSIM and ATMOS instruments flew on Spacelab 2 and 3 (1985), respectively. The SSBUV instrument has now flown a total of 8 times; three prior to the ATLAS 1 flight, once between ATLAS 2 and ATLAS 3, and once subsequent to the ATLAS 3 flight. The ESCAPE instrument, a student-led payload from the University of Colorado, made its first space flight on ATLAS 2, and the CRISTA and MAHRSI instruments, which flew aboard the German ASTRO-SPAS satellite that was deployed and retrieved from the Space Shuttle during the mission, made their initial flights during the ATLAS 3 mission.

Only subsets of the ATLAS payload could operate simultaneously, as the instruments did not have independent pointing capability. Thus, the Space Shuttle provided the pointing through control of its attitude. Typically, the payload bay was either pointed down towards the Earth, allowing the atmospheric chemistry instruments to operate, or to the sun, allowing the solar instruments to operate. The ATMOS instrument makes its measurements through the technique of infrared absorption at solar occultation, and thus obtained data at no more than two latitudes per orbit; the latitudes varied for each mission because of different launch times (these regions are shown in Table 2). The launch time for the ATLAS 2 and ATLAS 3 missions were chosen to allow for measurement of high-latitude sunrise occultations at high latitudes in the spring hemisphere (Northern Hemisphere for ATLAS 2, Southern Hemisphere for ATLAS 3) so that detailed

measurements of the trace constituent composition of the remaining polar vortices could be sampled. The MAS instrument measured out the side of the Shuttle, and could get nearly complete coverage of one hemisphere (up to approximately 80 degrees latitude) while getting partial coverage of the other (to approximately 30 degrees latitude) depending on whether the Shuttle was flying forwards or backwards.

Several important points to come from the missions related to the stratosphere include the following (results more closely associated with mesospheric and thermospheric science are not included in these highlights):

1. The three ATLAS missions were all highly successful from the standpoint of instrument operations. The only major failure was that of the MAS instrument on ATLAS 3, and that came after nearly a day of data. This came sufficiently far into the mission that the MAS team was able to get nearly complete coverage over the Northern Hemisphere. The CRISTA and MAHRSI instruments, which made their first flights during the ATLAS 3 mission, worked quite well, together with the ASTRO-SPAS satellite. There was a data downlink problem during the ATLAS 2 mission that affected the data from the ATMOS instrument, but its on-board recorder, which was flying as a test during the mission, allowed for recording of a significant number of observations, and data recovery for the mission was well above expectations. The Shuttle environment appeared to be quite adequate for most of the instruments on the three missions. There was some contamination in the payload bay during the first ATLAS flight, but additional steps were taken in preparing for the subsequent flights to protect the cleanliness of the payload bay, and these were successful. The flexibility of the Shuttle and Spacelab systems became very apparent in the missions, as several observations that had not been planned before the mission were carried out such as lunar viewing and collaborative observations between SSBUV and MAHRSI.

2. The three ATLAS missions covered a significant range of atmospheric and solar conditions. Three particular parameters had significant variation over the course of the mission:

   a) *Atmospheric aerosol loading*: The Mt. Pinatubo eruption in June 1991 led to the formation of a significant aerosol burden in the stratosphere. This was particularly severe during the ATLAS 1 mission, when most of the ATMOS occultations could not penetrate into the lowest part of the stratosphere because of the degree of aerosol extinction. Given the approximate lifetime for stratospheric aerosols of 1 year and the 2.5-year interval between ATLAS 1 and ATLAS 3, there was a significant reduction in aerosol loading during this period, so much that during the latter flight many ATMOS occultations penetrated into the upper troposphere. Differences in the effects of heterogeneous chemical processes which occurred on stratospheric aerosol particles are evident in the data from the three ATLAS flights (especially in northern mid-latitudes sampled during both ATLAS 1 and ATLAS 3). The ATMOS instrument had sufficient spectral coverage that some information about the composition of the aerosol particles during the ATLAS 1 mission could be obtained.

   b) *Atmospheric ozone amounts*: The stratospheric ozone amounts were significantly below climatological amounts during the ATLAS 2 flight. This flight occurred during the post-Pinatubo period of ozone depletion (mid-1992 to early 1994) thought to be caused by

heterogeneous reactions occurring on the enhanced sulfate aerosol layer. The SSBUV instrument was able to clearly show decreases in total ozone amounts between the ATLAS 1 and ATLAS 2 flights that were consistent with expectations based on other sources of data, notably Total Ozone Mapping Spectrometer (TOMS) data.

c) *Solar activity*: Solar activity decreased significantly from the ATLAS 1 to the ATLAS 3 flight, as measured by both the Mg-II index obtained using the Solar Backscatter Ultraviolet (SBUV/2) instrument aboard the NOAA 11 operational meteorological satellite, and the F10.7 cm flux measured from the ground. These differences in solar activity were apparent in both the total solar irradiance and spectrally resolved solar irradiance measurements made by the ATLAS payload. For example, the SSBUV instrument reported an approximately 5% decline in solar output near 200 nm between the ATLAS 1 (March 1992) and ATLAS 3 (November 1994) flight.

3. The high-latitude springtime measurements using the ATMOS instrument were highly successful in that the ATMOS observations were made both inside and outside the remnant polar vortices which were present during these flights (Northern Hemisphere in ATLAS 2, Southern Hemisphere in ATLAS 3). The ATMOS measurements showed clear differences in the trace constituent composition across the vortex boundary, and showed evidence for significant descent inside the vortices. Estimations of descent amounts compared favorably to those made previously on the basis of other measurements. Profiles obtained from the ATLAS instruments, particularly from ATMOS, showed significant differences in profile structure between the tropics, mid-latitudes, and high latitudes. These are consistent with expectations based on knowledge of atmospheric dynamics and measurements from other platforms, notably UARS. Evidence for significant wintertime descent at high latitudes was also obtained from the MAS instrument in the ATLAS 1 flight, when water vapor profiles measured at high northern latitudes showed clear evidence of descent in the stratosphere and mesosphere, even though the polar vortex at high latitudes had broken up prior to the mission. These latter results also suggest that there is a significant degree of isolation in the polar winter mesophere.

4. The ATLAS measurements were very useful in the comparison with other space-based measurements. Key comparison targets were UARS, the SBUV/2 instruments flying on the NOAA operational meteorological satellites (notably NOAA 11, but also NOAA 9, whose on-board calibration system did not work properly and for which such comparison measurements are particularly important), and solar irradiance measuring instruments aboard the European Retrievable Carrier (EURECA), which was deployed from and subsequently retrieved by the Space Shuttle and whose period of operation overlapped the ATLAS 2 mission. The SSBUV measurements from these flights were also used for comparison with the TOMS instruments that flew aboard NASA's Nimbus 7 satellite (ATLAS 1 and 2) and a Russian Meteor-3 satellite (all three missions). The contributions to UARS validation were significant, including the comparison of the ATLAS spectrally resolved ultraviolet measurements with those made from UARS, and the ATMOS comparisons with the trace constituent data obtained from the atmospheric chemistry instruments aboard UARS, especially for constituents such as CF_2Cl_2 and N_2O_5, for which there are very few sources of independent data over a broad altitude range. Comparisons of MAS and UARS Microwave Limb Sounder (MLS) data showed generally good agreement over a broad range of latitudes between the two

instruments. This was true for all three MAS flights. Excellent consistency was also found between the total solar irradiance measurements made with the SOLCON instrument and related instruments on other platforms.

5. Comparison of ATMOS data obtained from the ATLAS missions with those from the Spacelab 3 mission, which took place some 9.5 years before the ATLAS 3 mission (April-May 1985 vs. November 1994, both of which obtained data in the mid-latitude Northern Hemisphere) conclusively demonstrates the long-term change in the composition of several halogen-containing stratospheric trace constituents. The growth in upper stratospheric HCl and HF between the first and last ATMOS flight was on the order of 40 and 100%, respectively. Long-term increases in lower-middle stratospheric amounts of other constituents, such as SF_6 (8.0 ± 0.7%/year), $CHClF_2$ (8.0 ± 1.0%/year), and CF_4 (1.6 ± 0.6%/year), were also observed, while for other constituents, statistically significant increases were not observed (e.g., OCS, 0.1 ± 0.4%/year, HCN 1.0 ± 1.0%/year).

6. The first space-based measurement of diurnal variation of ozone profile through the stratosphere and mesosphere was reported based on data obtained with the MAS instrument. Results from the ATLAS 2 mission for 55°S show that significant percentage differences, with larger ozone amounts being observed at night, are found above approximately 50 km. The nighttime mid-mesosphere profile has an enhancement in ozone not seen in the daytime profile. The largest absolute difference between day- and night-time amounts is 1 ppmv just above 65 km; this difference decreases up to the daytime detection limit for ozone at 75 km. This behavior has been suggested by atmospheric models, but has not been seen by ground-based studies of mesospheric ozone made using microwave instrumentation because of the lack of vertical resolution of the latter technique.

7. An analysis of measurements of chlorine-containing species obtained using the MAS and ATMOS instruments shows that current models of stratospheric chemistry based on measured rates of chemical reactions do not adequately represent the partitioning of chlorine compounds in the upper stratosphere. In particular, the models appear to underpredict amounts of HCl and overpredict $ClONO_2$ and ClO. An additional process which leads to HCl formation, whose rate peaks at approximately 40 km, appears to be necessary.

8. A near coincidence between several ATMOS occultations during the very beginning of the ATLAS 3 flight and data obtained from the ER-2 at the very end of the Airborne Southern Hemisphere Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) campaign showed good agreement between data obtained in the lower stratosphere for most constituents compared. Although the agreement between the ATMOS and ER-2 observations is less clear for certain constituents (e.g., CO, HCl, CCl_4), there do not appear to be any glaring inconsistencies given the combined error bars on the two sets of measurements.

9. The ATLAS flights provided the first near-global information about the isotopic distribution of trace constituents in the stratosphere. These include the $^{18}O/^{16}O$ ratios in ozone and the D/H ratios in H_2O and CH_4. The results show that there is no significant vertical or latitudinal variation in the observed enhancement in heavy (mass-50) ozone, and show consistent evidence for greater enhancement in the asymmetric isomer ($^{16}O^{16}O^{18}O$) than the symmetric isomer ($^{16}O^{18}O^{16}O$). CH_3D was shown to enter the stratosphere with an average mixing ratio

of $9.9 \pm 0.8 \times 10^{-10}$, corresponding to a deuterium depletion of $7.1 \pm 7.4\%$ relative to standard-mean ocean water (one standard deviation). However, lower stratospheric water is found to be highly depleted in deuterium ($67 \pm 8\%$), which is less depleted than would be expected for upward transport by simple ascent, suggesting that the bulk of the water vapor entering the stratosphere must be carried by rapid convection to at least upper tropospheric levels.

10. The excellent agreement between the measurements from three spectrally resolving solar instruments (SUSIM, SOLSPEC, SSBUV) during the first ATLAS flight provides clear demonstration that the absolute solar spectral irradiance in the middle ultraviolet is now well known. These three instruments had all been calibrated against independent standards, and were recalibrated after the flights (as well as having onboard calibration systems). The mean solar ultraviolet spectral irradiance measured during the ATLAS 1 mission was within 3% of that measured by the two UV spectral irradiance measurements (SOLSTICE, SUSIM) aboard UARS. The total solar irradiance measurements made by the SOLCON instrument were shown to be slightly affected by the density of air at Shuttle altitudes, in a way which is consistent with that expected based on models of upper atmospheric density.

11. Excellent progress is being made in the analysis of CRISTA and MAHRSI data. Comparisons of data from these instruments with appropriate correlative data, including that from UARS and from ground-based data obtained during the STS-66 mission, indicate reasonable accuracy. Quantitative statements about most of these data cannot yet be made, however. The high horizontal resolution information on stratospheric trace constituents provided by CRISTA should prove very informative about small-scale features in their distributions. MAHRSI hydroxyl profiles have been retrieved to a lower limit of 45 km, and initial results suggest that there is some inconsistency between the observed lower and middle mesospheric OH distributions and those expected on the basis of observations of other species (e.g., water vapor) and laboratory rates for HO_x chemistry.

The largest collection of results from ATLAS are published in two special sections of *Geophysical Research Letters* - 19 March 1993 (ATLAS 1 only) and 15 August 1996 (results of all three flights). Numerous other publications detailing the results of these missions exist already in the peer-reviewed literature.

TABLE 1. THE ATLAS PAYLOAD AND CO-MANIFESTED INSTRUMENTS

Instr. Type	Instrument	Acronym	PI	Inst.	1	2	3
TSI	Active Cavity Radiometer Irradiance Monitor	ACRIM	R. Willson	JPL	x	x	x
TSI	Measurement of the Solar Constant	SOLCON	D. Crommelynck	IRMB	x	x	x
SSI	Solar Spectrum Measurement	SOLSPEC	G. Thuillier	SAC	x	x	x
SSI	Solar Ultraviolet Spectral Irradiance Monitor	SUSIM	G. Brueckner	NRL	x	x	x
CHEM	Millimeter-Wave Atmospheric Sounder	MAS	G. Hartmann	MPIA	x	x	x
CHEM	Atmospheric Trace Molecule Spectroscopy	ATMOS	M. Gunson	JPL	x	x	x
CHEM/SSI	Shuttle Solar Backscatter Ultraviolet	SSBUV	E. Hilsenrath	GSFC	x	x	x
CHEM	Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere	CRISTA	D. Offermann	BUGW			x
CHEM	Middle Atmosphere High Resolution Spectrographic Investigation	MAHRSI	R. Conway	NRL			x
SSI	Experiment for the Sun for Complementing the ATLAS Payload and for Education	ESCAPE	E. Hansen	U. Colorado		x	x
CHEM	GRILLE Spectrometer	GRILLE	M. Ackerman	IASB	x		
M/T	Imaging Spectrometeric Observatory	ISO	D. G. Torr	UAH	x		
M/T	Atmospheric Lyman Alpha Experiment	ALAE	J.-L. Bertaux	SAC	x		
M/T	Atmospheric Emission Photometric Imaging	AEPI	S. Mende	LPARL	x		
PLASMA	Space Experiments with Particle Accelerators	SEPAC	J. Burch	SWRI	x		
PLASMA	Energetic Neutral Atom Precipitation	ENAP	B. Tinsley	UT Dallas	x		
ASTRO	Far Ultraviolet Space Telescope	FAUST	S. Bowyer	UC Berkeley	x		

Abbreviation Key - Instrument Type:

ASTRO	Astrophysics
CHEM	Atmospheric Chemistry
M/T	Mesosphere/Thermosphere
PLASMA	Plasma Physics
SSI	Solar Spectral Irradiance
TSI	Total Solar Irradiance

Abbreviation Key - PI Institution

GSFC	Goddard Space Flight Center (US)
IASB	Inst. d'Aeronomie Spatial de Belgique (Bel.)
IRMB	Inst. Royal Meteor. de Belgique (Belgium)
JPL	Jet Propulsion Laboratory (USA)
LPARL	Lockheed Palo Alto Res. Labs. (USA)
MPIA	Max Planck Inst. fur Aeronomie (Germany)
NRL	Naval Research Laboratory (USA)
SAC	Service d'Aeronomie du CNRS (France)
SWRI	Southwest Research Institute (USA)
UAH	University of Alabama in Huntsville (USA)

TABLE 2. SUMMARY OF ATLAS FLIGHTS

Flight Number	Shuttle Flight	Launch	Landing	Solar Occult Location	Comments
1	STS-45	3/24/92	4/2/92	SR 30°S - 30°N SS 20°S - 55°S	Reduced measurement time was available for atmospheric science and solar meas.; 9 months after Mt. Pinatubo eruption led to very high aerosol loading
2	STS-56	4/8/93	4/17/93	SR 63°N - 69°N SS 20°S - 50°S	Downlink difficulty meant only usable ATMOS occultations were stored onboard; flight was during period of post-Pinatubo ozone depletion
3	STS-66	11/3/94	11/14/94	SR 65°S - 72°S SS 5°N - 50°N	MAS instrument obtained only limited data due to hardware failure; flight came during period of low solar activity

SECTION E

ASHOE/MAESA END-OF-MISSION STATEMENT

SUMMARY OF PRELIMINARY RESULTS

This statement summarizes the observations and preliminary interpretations of the science team for Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA). ASHOE/MAESA was sponsored by NASA's Upper Atmosphere Research Program and by NASA's High Speed Research Program; the National Oceanic and Atmospheric Administration (NOAA) and National Science Foundation (NSF) contributed substantially, as did the meteorological services of New Zealand, Australia, United Kingdom, and those signatory to the convention governing the European Centre for Medium-Range Weather Forecasts (ECMWF). The mission was designed to address questions about the causes of the year-round mid-latitude ozone loss observed in the Southern Hemisphere in the last 15 years and, in particular, the relative roles of vortex air transported to mid-latitudes and *in situ* loss induced by heterogeneous chemistry on sulfuric acid aerosols. These questions are important for the general understanding of the composition of the lower stratosphere and its consequent effects on the radiative balance of the atmosphere and, hence, for the assessment of the potential environmental effects of stratospheric aircraft upon this balance, a goal also served by the flights studying the exchange of air between the tropics and mid-latitudes of both hemispheres. More detailed analyses will follow during the coming months and years. There will be continuing comparison of these results with those from previous missions, including the 1987 Stratosphere Troposphere Exchange Program (STEP), the 1987 Airborne Antarctic Ozone Expedition (AAOE), the 1987 Airborne Arctic Stratospheric Expedition (AASE), the Second Airborne Arctic Stratospheric Expedition (AASE-II) in 1991-1992, and the Stratospheric Photochemistry, Aerosol and Dynamics Experiment (SPADE) in November 1992 and May 1993. Because this document represents a preliminary view of what the observations mean, it cannot be referenced in the scientific literature.

Flights of the NASA ER-2 high-altitude aircraft, carrying as many as 16 instruments, provided new observations to diagnose the chemistry, physics and fluid motion of air in the lower stratosphere. Measurements span the period from February to November 1994, and the region from the edge of Antarctica at 70°S to upper Canada at 60°N, in conjunction with observations from the ground, balloons, and satellites. Most measurements were in the Southern Hemisphere and in the tropics; the former was studied using *in situ* techniques over the entire evolution of the winter vortex, and the latter was so investigated for the first time.

Operation

The observations are based primarily on 45 flights of the NASA ER-2 high-altitude aircraft. For most flights, the ER-2 carried 16 instruments to measure the abundances of reactive and inert trace gases, aerosols, temperature, pressure, winds, ultraviolet light, and temperature profiles. For flights specifically designed to study dynamics and radiation, some of the trace gas instruments

were removed and an instrument that measures infrared radiation was added. Of the 45 flights, 26 were from Christchurch, New Zealand; 5 were from Barber's Point, Hawaii; and 6 were transits between New Zealand, Fiji, Hawaii, and California. Also included were two full-duration (8-hour) test flights north from Moffett Field in February, 5 short (2+ hours) test flights from Moffett Field between January and March and a northbound flight from Moffett Field in November 1994. Thirty-two flights had the full payload, 11 had the dynamics and radiation configuration, and 2 were test flights for individual instruments.

Observations from other instruments on the ground, balloons, and satellites provide valuable contributions to ASHOE/MAESA. Analyses of weather observations by the United Kingdom Meteorological Office (UKMO), ECMWF, United Kingdom Universities Global Atmospheric Modeling Project (UK UGAMP), the National Meteorological Center (NMC), and NASA's Goddard Space Flight Center (GSFC) aided flight planning and dynamical analyses. Satellite data from the Microwave Limb Sounder (MLS) and Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS), and the Total Ozone Mapping Spectrometer (TOMS) on Meteor-3 gave a global context for the *in situ* measurements of the ER-2. The GSFC Lidar and National Institute of Water and Atmospheric Research (NIWAR) column measurements from Lauder, New Zealand, and the MacQuarie Island ozone sondes provided valuable intercomparisons for aerosol and ozone measurements on the aircraft, extending the observations well above and below the aircraft. All these observations will be combined with those from the ER-2 for study.

Objectives

An over-arching mission objective, as laid out in the mission booklet, was to investigate the causes of long-term reductions of ozone in the wintertime mid-latitudes in the Southern Hemisphere that have been observed by ground-based measurements and satellites for the last 15 years. To meet this objective, ER-2 flights were designed to observe several aspects of ozone loss: the rapid decline of ozone each spring over Antarctica, the spread of ozone-poor and chemically perturbed air to mid-latitudes, and the activation of ozone-destroying chlorine directly in mid-latitudes by reactions on the sulfate aerosols and by polar stratospheric clouds (PSCs) in polar regions. Flights were designed to determine the rate of chemical removal of ozone by nitrogen, hydrogen, chlorine, and bromine chemical radicals, and to test our understanding of the processes that regulate the abundance of these reactive gases. Observations of tracers of lower stratospheric transport will permit study of the mixing of air between the mid-latitudes and tropics because this process helps establish the ozone distributions and rates of ozone change. The radiative transfer in the infrared was studied in order to observe the thermal structure of the lower stratosphere in and around the vortex, and to make more direct estimates of the diabatic cooling rates.

The evolution of the Antarctic polar vortex, with its circumpolar winds and low temperatures, was covered during the course of ASHOE/MAESA. The rapid loss of ozone, known as the ozone hole, that reaches its maximum extent early in October each year (i.e., during austral spring) appears mainly within this vortex. Measurements of trace gases and meteorological parameters were made early in the life cycle of the vortex (Deployment I in March-April), prior to the onset of cold temperatures; after the vortex formed and temperatures dropped below approximately 195 K, the formation temperature of polar stratospheric clouds (Deployment II in May-June); after the temperatures had dropped below ice saturation, when large-scale loss of the condensable vapors

HNO_3 and H_20 by sedimentation in PSC particles occurs (Deployment III in July-August); and when ozone was the most depleted (Deployment IV, October). The mid-latitude regions equatorward of the maximum in the polar night jet stream were also the subject of close observation and study.

The other objective of ASHOE/MAESA was to obtain measurements for the assessment of the potential atmospheric effects of a proposed fleet of future supersonic (High-Speed Civil Transport, HSCT) aircraft. ASHOE/MAESA addresses three of the most uncertain aspects of this assessment.

First is the transport by air motions of the exhaust from mid-latitudes, where most HSCTs will fly, to the tropics, where the exhaust could rise up and spread out to mid-latitudes at higher altitudes. Model calculations suggest that HSCT exhaust could efficiently destroy ozone above approximately 25 km altitude, while at 20 km the exhaust is currently expected to cause some local increases in ozone. Understanding the transport of air between the lower stratosphere where the HSCTs will fly and the middle stratosphere where the exhaust can do the most damage to ozone is essential. Observations of a large number of tracers with a range of lifetimes will provide a good opportunity to quantify transport processes.

Second, the HSCT exhaust is calculated to increase stratospheric water vapor and gaseous nitric acid, which are the main components of PSC). HSCT exhaust near the cold regions at the winter poles and the equator could therefore possibly increase the frequency and range of PSCs, and also the reactivity of gases on cold sulfate aerosols, which increases rapidly as the water content of the particles rises. Because chlorine is rapidly converted to its ozone-destroying forms on PSCs and cold sulfate aerosols by reactions of the reservoir gases on the particles, an increase in these clouds could result in increased ozone loss. The measurements of aerosol size distribution and refractive index will enhance quantitative knowledge of these processes.

Third, the uncertainties in the laboratory measurements of chemical reaction rates and products that are used in assessment models directly affect the uncertainty in the calculations of ozone loss expected for projected injections of HSCT exhaust. Measurements of concentrations of hydrogen, nitrogen, chlorine and bromine radicals, and their reservoirs and precursors made during ASHOE/MAESA provide a rigorous test of our understanding of processes which regulate the abundance of reactive gases in the stratosphere. The measurements allow quantification of the effects of current laboratory uncertainties and chemistry not represented in the models on the calculated concentrations of reactive gases. Observations taken over a wide range of latitudes, altitudes, seasons, time of day, and abundances of chlorine, bromine, and nitrogen chemicals provide a stringent test of the processes controlling reactive species.

An additional research effort was conducted through an opportunity to measure directly the chemical composition of the exhaust plume from a Concorde supersonic airliner as it approached Christchurch, New Zealand. Of the currently operating aircraft, the Concorde is the one most similar to the projected HSCTs. Measurements of the chemicals in its exhaust over a range of times after emission tests the validity of the ground-based measurements of the emission indices of pollutants for the Concorde. The measurements also test atmospheric chemistry for the polluted conditions of the exhaust plume.

SUMMARY OF OBSERVATIONS AND RESULTS

These unique observations of variations of long-lived trace gases (including ozone, H_2O, N_2O, CO_2, CH_4, CO, H_2, SF_6, and a wide range of CFCs) in the lower stratosphere will help define the transport and mixing of air among the polar, mid-latitude, and tropical regions of the stratosphere and the troposphere. Observations and models indicate that the transport of polar air, primed for ozone loss, occurs as filaments that are shed into the mid-latitudes. Studies underway seek to quantify the mid-latitude ozone loss that results from this mixing process. Tropical stratospheric air is also observed to be shed as filaments into mid-latitudes. The aircraft observations suggest that mid-latitude air mixes into the outer tropics from 23.5° to about 10° latitude, with the inner equatorial region showing signs of air which entered the stratosphere more recently from below. The extent to which the outer tropical air can ascend to higher altitudes is crucial in the context of the potential effects of HSCT exhaust. Calculations show that such exhaust will destroy ozone if it gets to higher altitudes. These observations provide new insight on the transport of air both in the stratosphere and between the stratosphere and troposphere.

The ASHOE/MAESA observations will improve the understanding of the processes that lead to the Antarctic ozone hole and to ozone loss at mid-latitudes. These processes include the formation of PSCs, the conversion of chlorine from its reservoir forms to its ozone-destroying reactive form on cold sulfate aerosols, and of the return of chlorine to the inactive forms after all ozone is destroyed inside the ozone hole. The transport mechanisms that redistribute the effects of these chemical processes will also be better understood. There will be a better understanding of the detailed mechanisms of the processes, which will help to improve numerical models used to simulate the stratosphere.

These observations, when compared to theoretical models, demonstrate a generally good understanding of the photochemistry in the lower stratosphere for the altitudes, latitudes, and seasons sampled during ASHOE/MAESA. The main disagreement between observation and current model calculation is the amount of chlorine in the form of HCl in the Northern Hemisphere during 1991 to early 1993; for both the Northern and Southern Hemispheres in 1994 the agreement is good. Generally, agreement is far better than expected from the stated errors in the measurements and the model parameters.

The simultaneous measurements of the reactive hydrogen, reactive chlorine, and reactive bromine show conclusively that these species destroy ozone faster in the lower stratosphere than does reactive nitrogen, in the chlorine-laden stratosphere of the 1990s. Reactive nitrogen is now thought to be dominant only higher in the stratosphere, above altitudes sampled by the ER-2. Thus, the calculated effect of HSCT exhaust on ozone is to produce small ozone increases in the lower stratosphere. The importance of reactions on sulfate aerosols that convert reactive nitrogen to reservoir forms is confirmed for a stratosphere with the low aerosol amounts characteristic of the period three or more years after a major volcanic eruption.

OBSERVATIONS AND RESULTS FROM ASHOE/MAESA

The structure of this section is based on a consideration of three latitude regimes: polar, mid-latitude, and tropical. A separate section is devoted to the Concorde exhaust encounter. Statements are presented as separate paragraphs under each heading.

Polar Region

Ozone in the Antarctic polar vortex during October was substantially depleted, just as in the previous two years. Preliminary minimum ozone values reported by Meteor-3 TOMS were 90 Dobson Units (DU) and the average areal extent of intense ozone loss was about 23 million km^2, slightly larger than in 1992 and 1993, and almost twice the size of Antarctica. Ozone loss in the Antarctic polar vortex has now been severe in seven of the last eight years.

The aircraft observations of ozone, tracers, and radicals provide a high-quality set and span a wide range of latitudes and altitudes between 16 and 21 km in the lower stratosphere over the whole period from March to October. They provide the database to examine the chemical loss of ozone and its relationship to diabatic cooling and the transport it induces in the region of the polar night jet stream and the vortex. The greatest ozone losses in and near the vortex occurred at the lower altitudes in the region (16 to 20 km) sampled by the ER-2.

Mean temperatures and other gross average indicators of dynamical activity associated with the Antarctic polar vortex were near the average values for the last 15 years, implying that observations from ASHOE/MAESA are representative of conditions in the recent past. These indicators include the stratospheric zonal mean winds and heat flux at 60°S and zonal mean temperature gradient. Minimum temperatures, important for PSC activity, were slightly lower than average by a few degrees for June through October. Temperatures less than 195 K persisted at 70 mbar within the vortex into the third week of October, and at 100 mbar into early November.

Observations and model calculations demonstrate that air is transported out of the vortex as filaments that are sheared from the vortex edge and become thinner with time. The shedding of filaments was observed during all deployments, but was most intense in October. Studies of observed variations in the winds near the vortex edge will define the importance of smaller scale fluctuations for the exchange of air between the polar region and mid-latitudes. There is on some flights preliminary evidence for a possible temperature signature associated with filaments from the vortex edge. Preliminary studies show examples of vertically laminated tracer structures correlated with the *in situ* winds. Some of these wind variations are undular, suggesting a role for gravity and inertia-gravity waves in cross-vortex transport. Turbulence was comparatively weak at the vortex edge as compared to the lower stratosphere over New Zealand.

Observations of ClO, HO_2, OH, NO, and NO_2 were made in the air in and around the polar vortex during all four deployments. Analysis of these observations will allow us to quantify the role of heterogeneous reactions on cold sulfate aerosols in regulating the abundance of radicals. Simultaneous observations of HO_x and ClO will allow us to distinguish between the role of two processes that lead to production of reactive chlorine on sulfate aerosols: $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$ and $HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$, since the first of these produces HO_x more efficiently than the second. Laboratory studies suggest that $ClONO_2 + H_2O$ on sulfate aerosols is important when the temperature is below about 200 K. This process will probably become more important at higher temperatures with the addition of water vapor and NO_y from HSCT exhaust. Measurements made in type I PSCs at the vortex edge during late July challenge the commonly accepted notion that such clouds consist entirely of particles of nitric acid trihydrate (NAT). As in the Arctic, the main cloud did not appear until temperatures were 2 to 3 K colder than NAT saturation.

The clouds appeared to be made up of externally mixed particles, and could contain both liquid and frozen particles of various hydrates and ternary mixtures of water, sulfuric acid, and nitric acid. Ice crystals may have been present. Surface areas of aerosols appeared to be much lower in cloud-free vortex air which had earlier been colder than the frost point.

Tracer mixing ratios inside the vortex appeared to be higher than those encountered at similar altitudes and latitudes during the 1987 AAOE mission from Punta Arenas. Intense denitrification and dehydration were not encountered in horizontal flight above 16 km, except on one flight in early October when water vapor dropped sharply 7° of latitude poleward of the wind maximum; in 1987 the loss of condensable vapors was mostly evident closer to the wind maximum. There was no large asymmetry (30%) of water vapor between the hemispheres outside the vortex, a feature which was observed in 1987.

Preliminary measurements of molecular hydrogen during August and October constrain its value at flight altitudes to between 0.45 and 0.70 parts per million by volume (ppmv). There is a low-amplitude inverse correlation between H_2 and CH_4 in the lower stratosphere, indicating that a modest fraction of the methane molecules which originally entered the stratosphere are not converted to water vapor.

Greater than expected abundances of NO_y, caused by evaporation at ER-2 levels of particles sedimenting from a higher altitude, were observed in early June near the vortex edge at about 16 km. Denitrification (irreversible removal of NO_y by particle growth and sedimentation) was observed in mid-winter (July) and later, mainly at and below 16 km. The amount of denitrification is an important process for the complete removal of ozone observed in the Antarctic polar vortex. Observed dehydration was minimal in early August; in early October, intense dehydration occurred about 7° latitude south of the vortex edge at cruise altitudes (18 to 20 km). At and below about 16 km, some obviously dehydrated air was observed further equatorward.

Denitrification was observed on some flights at about 16 km in early June and early August, with no accompanying dehydration. The two processes are thus shown to be independent over Antarctica. Dehydrated air in August and October was also denitrified.

Large increases in ClO and decreases in HCl were observed after the occurrence of PSCs. Beginning in early June, for air which had been at temperatures below 195 K, ClO was observed to increase to between 700 and 900 parts per trillion by volume (pptv) and HCl to decrease by amounts up to 1.5 parts per billion by volume (ppbv). This air was in the outer regions of the vortex; penetration to the inner regions, where higher ClO abundances were present, was not possible given the combination of vortex motion, airfield weather, and flight duration. Activated chlorine in the form of enhanced CIO was seen in the polar vortex on four flights. Loss of HCl was seen on other flights as well, because the instrument concerned was on the dynamics and radiation flights. These observations of ClO and HCl, and the stoichiometry for HCl loss vs. ClO + $2Cl_2O_2$ production, show in detail the role of PSCs in creating enhanced levels of ozone-destroying reactive chlorine.

The observations confirm that ClO_x and BrO_x catalytic chemistry dominates ozone loss in the polar vortex. Although it had been suggested that OH and HO_2 might have a significant role for polar ozone loss, the observations of small OH and HO_2 abundances demonstrate an insignificant role for OH and HO_2 in ozone loss inside and around the vortex for fall through to spring.

Polar air nearly devoid of ozone was sampled *in situ* for the first time inside the vortex near the 400 K potential temperature surface (about 16 km altitude) on 10 and 13 October. Mid-October is late in the period of severe ozone depletion over Antarctica. This air contained little ozone (<0.4 ppmv), little or no ClO (<100 pptv), high NO (1 ppbv), low NO_y (2 ppbv), and HCl equivalent to estimates of total inorganic chlorine (2.6 ppbv). The almost total loss of ozone creates a condition where chlorine is shifted rapidly from ClO to HCl via the reaction of Cl with CH_4, and NO_y is shifted into NO. Thus, HCl was observed to be the dominant remaining chlorine species, whereas in the Arctic, with smaller ozone loss, $ClONO_2$ has been observed by others to be in this role. The implications of these interhemispheric differences in the final phases of the polar vortices on ozone loss at mid-latitudes are being examined.

The dynamics and radiation payload provided evidence for a layer of warm air in the 14- to 17- km region at the base of the vortex which was not well-reproduced in meteorological forecasts and analyses. Preliminary estimates of diabatic cooling rates in the polar night jet stream and in the vortex between the tropopause and 19 km showed somewhat larger cooling rates than those produced by numerical model calculations. At the latitudes of the polar night jet stream and the vortex, the lower stratospheric air below about 60 mbar (the approximate cruise altitude of the ER-2) during the dynamics and radiation flights was up to 5 K colder than the temperatures in global meteorological analyses and in low vertical resolution soundings from operational satellites.

Observations from the UARS satellite made by the MLS and HALOE instruments were provided to the aircraft site in Christchurch. The Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument on the Space Shuttle made measurements coincident with the ER-2 in early November. Preliminary intercomparisons with the ER-2 for all these instruments are encouraging, and lend both powerful support and a global context, including altitudes above the aircraft, to the *in situ* measurements.

Middle Latitudes

The fast photochemistry of the lower stratosphere appears to be well understood for the altitudes, latitudes, and seasons that were sampled by the ER-2 during ASHOE/MAESA and SPADE. This ability to test the photochemical chain reactions is a direct result of careful, simultaneous measurements of a number of trace gases and meteorological parameters on the same platform, a capability which has not existed previously. The observed NO, OH, HO_2, and ClO are well simulated by a model that uses measured long-lived species as input data. Agreement is generally far better than expected from the stated errors in the measurements and the model parameters. This understanding greatly increases confidence in the chemistry incorporated into assessments models for studying the effects of HSCTs.

However, there is an important deviation from the generally good agreement between observation and model calculation: the HCl/Cl_y ratio in the Northern Hemisphere. In 1991/1992 this ratio was observed to be approximately 0.35+0.1 and in 1993 about 0.45+0.15, these fractions being only about 60% of model predictions. However, in four flights at the beginning and end of ASHOE/MAESA in February and November 1994, the measured HCl/Cl_y ratio was 0.55+0.15, in agreement with model predictions. Also, data from several flights in the Southern Hemisphere, where the air had not recently been below 195 K, showed measured values of HCl/Cl_y ranging from 0.6 to 0.9. The Cl_y budget, which is constructed from measurements of organic chlorine,

HCl and ClO, and $ClONO_2$ inferred from ClO and NO, was balanced in the Southern Hemisphere in 1994, but not in the Northern Hemisphere for 1991 through early 1993. The interhemispheric asymmetry in the HCl/Cl_y ratio, and the apparent evolution with time of the Northern Hemispheric ratio may be associated with the enhanced particle surface areas resulting from the eruption of Mt. Pinatubo, but the responsible mechanism is not known.

Filaments of both polar and tropical air are observed at mid-latitudes for potential temperature surfaces between 340 K and 520 K (roughly 14 to 20 km altitude), as they were during AASE II and SPADE. These filaments, which are contorted into thin sheets by wind shear, are often predicted by contour advection and trajectory dynamical models. They may be a dominant way that air is transported among the polar region, mid-latitudes, and tropics. The combination of *in situ* observations and these new advanced modeling tools will provide additional insight into transport processes.

The amount of aerosol in the stratosphere has decreased steadily since the eruption of Mt. Pinatubo. During ASHOE/MAESA, the aerosol surface area dropped from 2×10^{-8} cm^2 cm^{-3} to less than 1×10^{-8} cm^2 cm^{-3}, with even lower values seen on 8 and 10 August near and inside the vortex. These values are comparable to background values observed before the eruption of Mt. Pinatubo. Thus, the influence of aerosols on the trace chemical species and on ozone loss is less now than it was for the previous missions: AASE-II in 1991/1992 and SPADE in 1993. The expected chemical response of the partitioning with in the nitrogen, halogen, and hydrogen chemical families for this range of aerosol surface areas has been confirmed for all latitudes. Because HSCT exhaust is calculated to increase the amount of ozone in the lower stratosphere in the presence of these aerosols, this confirmation is important.

Observations of HO_2, ClO, BrO, and NO during ASHOE/MAESA show that the HO_x and ClO_x catalytic cycles dominate ozone destruction globally in the lower stratosphere. These results are similar to those from SPADE, but extend over a wide range of latitudes and seasons. On this basis, small increases in NO_y, such as those that might occur from HSCTs, would decrease ozone loss in the lower stratosphere.

OH and HO_2 have been measured in the upper troposphere for the first time, along with NO, NO_y, ozone, CO, and CH_4. Analysis of these measurements, made during ascent, descent, and dives of the ER-2 into the troposphere, provides fairly complete first tests of the photochemistry for this region. Knowledge of the photochemistry of the upper troposphere is important for global climate change and for the effects of the current fleet of subsonic aircraft.

Tropics

Prior to ASHOE/MAESA, many gases that indicate atmospheric motion were either poorly measured or unmeasured in the tropics. A number of gases were observed during ASHOE/MAESA in both the tropics and mid-latitudes, including N_2O, CO_2, CO, H_2O, CFC-11, CH_4, SF_6, and ozone. These gases have different trends and CO_2, H_2O, CO, and ozone have seasonal variations as well. The variation of the relationships among these gases with season, latitude, and altitude, especially when compared to tropospheric values, gives new information about transport into the stratosphere and between the stratosphere and troposphere.

The relationships among these tracers is distinctly different in the tropics and mid-latitudes. The tropical regime defined by trace gases is about 15° to 20° wide in latitude. The low value for NO_y/O_3 previously observed during STEP and AAOE in 1987 in the tropical regime was confirmed. Long-lived tracers approach tropospheric values in this region.

The tropical observations in late October showed a layered structure in the vertical near the equator between 16 and 20 km, which was present in H_2O, NO_y, CO_2, and aerosols; the minimum water was collocated with the tropopause. These measurements will shed new light on the entry and dehydration of air at the equatorial tropopause.

Poleward of the changes in the tracers, the values of NO_y/O_3 and long-lived tracers are observed to be intermediate between the observed values deep within the tropics and at middle latitudes. These observations suggest that information about mixing between the tropics and mid-latitudes can be obtained from analysis of these observations. This information is crucial for understanding the potential transport of HSCT exhaust in the upwelling of the tropics to the middle stratosphere, where it will chemically destroy ozone.

Because stratospheric CO_2 is a conserved tracer with little production in the stratosphere and both a trend and a seasonal variation in the troposphere, the propagation of the secular and seasonal changes into the stratosphere, first observed during SPADE in 1992/1993, gives an indication of both transport and mixing. Its variation in the stratosphere of both hemispheres was approximately in phase with the seasonal variation in the Northern Hemisphere troposphere in March/April from 61°N to 68°S. This behavior suggests that air enters the stratosphere in the tropics.

The NO and NO_y abundances are observed to increase, relative to expected values, in thin layers in the lower stratosphere and upper troposphere. The cause of these layers with enhanced NO_y is not yet known. However, understanding these features has implications for the NO_y budget in the lower stratosphere and upper troposphere and, thus, for the assessment of the effects of current subsonic aircraft.

The effects of enhanced albedo from high tropical clouds on the abundances of the reactive gases NO, OH, and HO_2 have been observed for the first time. Because the rates of chemical decomposition by sunlight are calculated and not measured for the stratosphere, these observations test these photolysis rates. The agreement is generally good between observed and calculated abundances of NO, OH, and HO_2, implying that the calculated rates are reasonably accurate.

Stratospheric Sampling of Concorde and ER-2

On 8 October 1994, off the northeast coast of New Zealand, the NASA ER-2 aircraft sampled the exhaust plume of a Concorde aircraft being operated supersonically by Air France. The ER-2, in each of three separate legs, sampled a 320-km path that was traversed by the Concorde over a 10-minute period. Each of the ER-2 legs required 30 minutes of sampling and were separated in altitude by about 1000 ft. The plume was encountered in the two legs at and below Concorde flight altitude.

Encounters with the Concorde exhaust plume were established by *in situ* observations of trace constituents made with instruments onboard the ER-2 as follows: carbon dioxide (CO_2), water vapor (H_2O), nitrous oxide (N_2O), carbon monoxide (CO), reactive nitrogen (NO, NO_2, NO_y), reactive hydrogen (OH, HO_2), and condensation nuclei (CN).

The plume was sampled on approximately 10 occasions with a duration that varied from 4 to 14 seconds. Instrument sampling rates varied from 0.3 Hz to 8 Hz corresponding to a spatial resolution between 600 and 25 m, respectively. The age of the plume as determined by the position of the encounter along the Concorde flight path varied from 10 to 70 minutes.

CO_2 reached peak values up to 2 ppmv above ambient values of 356 ppmv. The integrated change in CO_2 above background values is needed to relate other constituent observations to the quantity of fuel burned. Such background values are determined by using the measurement of N_2O, which is not produced in jet engines in sufficient quantities to be detected, and the strong correlation between N_2O and CO_2 observed in the background atmosphere. The amount of water vapor observed in the plumes was less than the 1:1 mole ratio of H_2O:CO_2 expected from complete combustion. The relatively slow response of the water vapor instrument is considered to be the cause of the low peak values.

CO is a product of incomplete combustion. In all plume encounters, no CO increase was observed to coincide with that of CO_2 and other species, whereas CO increases were found in previous ER-2 exhaust plume measurements.

Reactive nitrogen, NO_y, and the component species NO and NO_2, were observed in each encounter. The abundance of NO_y ratioed to the abundance of CO_2 yields the emission index (EI) of nitrogen oxides for the engine operating conditions. The values for the EIs will be calculable from these data, as they were for earlier encounters of the ER-2 with its own exhaust during SPADE. Measured ratios near unity for $(NO + NO_2)/ NO_y$ indicate that NO and NO_2 are the primary reactive nitrogen species in the exhaust plume up to an hour after emission.

CN are a measure of small particles emitted by the engine or produced from the condensation of gases in the exhaust. All plume encounters contained CN concentrations elevated significantly above background values of 6 to 18 cm^{-3}. In most encounters, a large fraction of the particles were completely volatilized at 192°C, consistent with sulfuric acid composition. The absence of a plume signal in other particle sizing instruments on the ER-2 indicates that particle diameters are smaller than 0.09 micrometers. Values found in the ER-2 exhaust were generally below 200 particles cm^{-3}.

Simultaneous measurements of OH and HO_2 were made during each encounter with a spatial resolution of 25 m. In the youngest plume samples, OH was found to increase and HO_2 to decrease. As the plume aged, the perturbation in OH decreased. The perturbation of the ratio of OH to HO_2 is consistent with the direct reaction of HO_2 with NO in the exhaust. The Concorde observations are similar to those made in the exhaust plume of the ER-2 aircraft in that they both implicate HONO as the source of OH in the exhaust plume. This is consistent with the time evolution of the HO_x signal in the Concorde samples and with observations of the ER-2 exhaust plume at night. It should be possible to calculate an EI for OH from the data; such a number will be a lower limit since all the nascent OH is assumed to be converted to HONO in the immediate wake of the aircraft.

As expected, no change in ozone was observed in the Concorde wake, if N_2O is used to infer background ozone values.

SECTION F

TOTE/VOTE END-OF-MISSION STATEMENT

The goals of the Tropical Ozone Transport Experiment (TOTE) and the Vortex Ozone Transport Experiment (VOTE) were to examine the stratospheric production of small-scale trace-gas filaments in the polar and tropical regions using upward-looking lidars flown onboard a DC-8 aircraft equipped with a suite of specialized instruments. The TOTE Mission was flown during December 1995, with most of the flights originating from Hawaii (two flights were made from Fairbanks, Alaska). The VOTE mission was flown from Fairbanks and Iceland, with a segment near Hawaii coincident with the Stratospheric Tracers of Atmospheric Transport (STRAT) aircraft mission. The major scientific findings are summarized below.

TOTE SUMMARY OF SCIENTIFIC RESULTS

- The initial part of the TOTE mission deployed from NASA Ames Research Center in Moffett Field, CA to Fairbanks, AK and then to the island of Oahu in Hawaii. In the polar region, sharp gradients in ozone were seen outside the vortex as we crossed polar vortex filament structures both approaching Fairbanks and during the cross vortex flight out of Fairbanks. The location of these filaments was predicted fairly well. There was no evidence of intrusions into the polar vortex.
- The DC-8 underflew the coldest part of the vortex; temperatures were cold enough to form nitric acid trihydrate (NAT), but only particles which did not depolarize the lidar return were observed. These were interpreted as hydrated sulfate aerosols. New theories of PSC (polar stratospheric cloud) formation suggest that the hydrated sulfate aerosols must first freeze at colder temperatures to provide nuclei before NAT can form. These observations are consistent with the new theories.
- The transit flight from Fairbanks to Hawaii showed that stratospheric ozone had significant variability in structure with 20 to 30% variations in the 25-km region. These structures were 1- to 2-km deep and 100- to 200-km long. Subsequent flights showed these structures were reproduced on turns, proving that they are not "noise" artifacts. Long-range (10- to 15-day) back trajectory calculations suggest that these structures are fossil filaments, and it is difficult to distinguish older filaments from newly formed ones. Further analysis shows that the time-averaging kernel for the ozone lidar will broaden these structures in the data, so it is not clear what the actual scale is for these features.
- Southward flights from Hawaii to the equator showed that the same mid-latitude-type variability seen on the flight from Fairbanks persists all the way into the tropics, even though ozone amounts increased steadily.
- Subvisible cirrus layers were observed south of Hawaii descending from the very lowest part of the stratosphere to below the tropical tropopause as the aircraft flew south. These layers were thicker at lower altitudes and seemed to have been advected northward from tropical

convection. They were identified as cirrus because of their high lidar backscatter, their depolarization, and because the layers merged into dense cirrus in the intertropical convergence zone. Low ozone was coincident with the stratospheric subvisible cirrus layers, suggesting that the layers had ascended from the troposphere. The subvisible cirrus was again observed by lidar on a second southward flight. Trajectory analysis revealed that the cirrus had formed very recently as a result of condensation of upper-level water vapor originating in the tropical west Pacific convective regions and then advecting north to warmer regions and then returning back to the colder tropics.

- *In situ* particle, NO_y, and NO observations through cirrus decks showed NO_y on cirrus particles. The amount of NO_y on the ice crystals was about 10% of the ambient gas-phase NO_y. This may be the first observation of heterogeneous chemistry on cirrus ice. Methane lidar observations of temperature showed good agreement with assimilation analysis, although there is some offset. Methane and water data showed variations which followed PV contours as expected theoretically.

VOTE SUMMARY OF SCIENTIFIC RESULTS

- Sharp gradients in ozone were seen again (see TOTE mission discussion) outside the vortex as the aircraft crossed polar vortex filaments during the local flights out of Fairbanks and the Iceland transit. The location of these filaments was predicted fairly well. There was some evidence of intrusions into the vortex as predicted.
- The DC-8 underflew the coldest part of the vortex on the transit to Iceland; temperatures were cold enough to form NAT, but no particles were observed. The Microwave Limb Sounder (MLS) measurements taken aboard the Upper Atmosphere Research Satellite (UARS) showed that the vortex appeared to be denitrified, which would explain the absence of PSCs.
- The transit flight from Fairbanks to Hawaii again showed (see TOTE section) that stratospheric ozone had significant variability in structure, with 20 to 30% variations in the 25-km region.
- Southward flights from Hawaii to the equator showed that the same mid-latitude-type variability we saw during TOTE though ozone amounts increased steadily. Subvisible cirrus layers were observed south of Hawaii as during TOTE. They were identified as cirrus because of their high lidar backscatter, their depolarization, and because the layers merged into dense cirrus in the intertropical convergence zone. The subvisible cirrus was also observed south of the equator, north of the Southern Tropical Convergence Zone.
- *In situ* particle, NO_y (all odd nitrogen species), and NO observations through cloud decks near Fairbanks showed NO_y on particles. This repeats an observation made during TOTE.
- Methane lidar observations of temperature showed good agreement with assimilation analysis. Methane and water data showed variations which followed PV contours as expected theoretically. Low methane was seen inside the polar vortex during the Iceland transit.
- A number of exhaust self-sample maneuvers were performed by flying in circles and descending 100' on each leg. In all cases elevated levels of H_2O, CO_2, NO_y, and sometimes NO were detected. At the end of the deployment, and in conjunction with the STRAT mission, the ER-2 high-altitude aircraft sampled the exhaust of the DC-8 as well as the ambient air. The

ambient air sampling allowed investigators to cross-calibrate the DC-8 and ER-2 instruments. Coincident measurements with the ER-2 for water, NO_y, NO, CO_2, and CO showed excellent agreement.

Comparison of ozone measurements in the polar region during TOTE with those made during VOTE showed significant ozone loss greater than 20% (December to early February).

Both TOTE and VOTE missions were extremely successful. The prediction of polar filaments was on target, which validates the conclusions drawn from contour advection and reverse-domain filling (RDF) calculations on the flux of material from the vortex to mid-latitudes. The prediction of tropical filaments was more problematic, probably reflecting the lower forecast capability in the tropics. The observations of tropical subvisible cirrus were new and exciting. And the exhaust self-sampling was a good prelude to the NASA Subsonic Aircraft: Contrail and Cloud Effects Special Study (SUCCESS) aircraft mission conducted in April 1996.

SECTION G

CHEMICAL KINETICS AND PHOTOCHEMICAL DATA FOR USE IN STRATOSPHERIC MODELING: EVALUATION NUMBER 12 OF THE NASA PANEL FOR DATA EVALUATION

RECENT CHANGES AND CURRENT NEEDS OF LABORATORY KINETICS

O_x Reactions

The kinetics of the O, O_2, and O_3 system are relatively well-established. However, the O + O_2 + M reaction remains of fundamental importance in atmospheric chemistry. This is because the extent of ozone destruction is determined by the relative rates of competing reactions such as O + O_3, O + NO_2, O + OH, and O + ClO. Additional studies of the ozone-forming reaction, or of its relative rate compared to the competing reactions, would be useful, especially at very low temperatures.

Reactions of Singlet Oxygen

$O(^1D)$ REACTIONS

The recommended rate coefficients for the $O(^1D)$ reactions correspond to the rate of removal of $O(^1D)$, which includes both chemical reactions and physical quenching of the excited O atoms. Details on the branching ratios and products are given in the notes.

The kinetic energy or hot atom effects of photolytically generated $O(^1D)$ are probably not important in the atmosphere, although the literature is rich with studies of these processes and with studies of the dynamics of many $O(^1D)$ reactions. The important atmospheric reactions of $O(^1D)$ include: (1) deactivation by major gases, N_2 and O_2, which limit the $O(^1D)$ steady state concentrations; (2) reaction with trace gases, e.g., H_2O, CH_4, and N_2O, which generate radicals; and (3) reaction with long lived trace gases, e.g., HCN, which have relatively slow atmospheric degradation rates. There are no data for the $O(^1D)$ + HCN reaction.

O_2 ($^1\Delta$ AND $^1\Sigma$)

Fourteen reactions of the ($a^1\Delta_g$) and ($b^1\Sigma^+_g$) excited states of molecular oxygen are reviewed. These states are populated via photochemical processes, mainly the UV photolysis of ozone and the reaction of $O(^1D)$ with O_2. Over the years they have been proposed as contributors to various reaction schemes in the atmosphere, but as yet no significant role in the chemistry of the stratosphere has been demonstrated. The fate of most of these excited species is physical quenching by means of energy transfer processes. In the few cases where chemical reaction occurs, it is indicated in the corresponding note.

HO_x Reactions

There have been no changes in the database for HO_x chemistry since the last evaluation. The $HO_2 + O_3$ reaction rate coefficient remains one of the most significant uncertainties in the HO_x system. High quality data at low temperatures are needed for this key reaction.

NO_x Reactions

There are no significant changes to the recommendations on NO_x reactions. The recommendation for the $HO_2 + NO$ reaction has been changed and the uncertainty factor reduced to reflect a new direct study of this reaction in the high pressure (several hundred torr) regime. The $NH_2 + NO$ and $NO + O_3$ reactions have been reevaluated resulting in a significant reduction in the uncertainty factors of both reactions.

Hydrocarbon Oxidation

The major update in this evaluation is the inclusion of the reactions of acetone and alkyl nitrates. In addition, several changes to the recommended values have been made in light of recent data.

The rate coefficient for the reaction of OH with CH_4 has been revised very slightly, based on recent work at temperatures close to 200 K. Even though the recommendation is in the form of an Arrhenius expression, the three parameter expression given in the note may better represent the data. It may be preferred in some cases.

There have been direct measurements of the rate coefficients for the reactions of many peroxy radicals with NO, and this database has been significantly improved. The current recommendations reflect the better database on peroxy radical reactions. The rate coefficient for the reaction of $CH_3C(O)O_2$ with NO has been measured directly and is now recommended. This recommended value also leads to a consistency, which was previously absent, in the ratio of the rate coefficients for the reactions of $CH_3C(O)O_2$ with NO and NO_2.

Even though there have been many studies on the reactions between peroxy radicals, the use of only UV absorption to measure the rate coefficients is still a limiting factor. All peroxy radicals have similar absorption spectra and cross sections. Therefore, deconvolution of the measured absorbances into changes in concentrations of individual reactants is not unambiguous. Use of peroxy radical detection by methods other than UV absorption would be very beneficial.

The reactions of OH with CH_3CN and HCN still require further study, because both the rate and mechanism are uncertain. Studies of larger (>C3) hydrocarbons, especially those containing oxygen, will be of interest in elucidating the hydrocarbon chemistry in the upper troposphere and the lower stratosphere. Such information is needed to assess the effects of aircraft emissions on ozone and climate as well as the general state of the upper troposphere.

Halogen Reactions

The kinetics database for homogeneous reactions of halogen species has been expanded since the previous evaluation. Rate coefficients for the reaction of OH with sixteen HFCs, HFOCs, and HCFCs have been added, increasing to forty-nine the number of potential alternatives to the fully

halogenated CFCs for which rate data for reaction with OH are now included. Rate coefficients for the reaction of chlorine atoms with many of these species are also included. Note that rate coefficient data for the reaction of these species with $O(^1D)$ are included in the $O(^1D)$ section of Table 1. More information on halocarbon degradation mechanisms in the atmosphere can be found in Francisco and Maricq [1995], Wallington *et al.* [1994], and WMO [1994]. There have been some changes in the recommendations for reactions included in the previous evaluation, in particular for reactions of OH with HFCs and HCFCs. With these additions and improvements, the kinetics database for homogeneous gas-phase reactions of halogen species appears to be well-established.

SO_X Reactions

The database on gas phase atmospheric sulfur chemistry has seen only minor changes in the recommendations for the reactions that were included in the previous evaluation. Minor expansion of this section continues in the area of reactions important in the atmospheric oxidation of reduced sulfur compounds of natural and anthropogenic origin. The database also continues to expand as more information becomes available on halogen atom and halogen oxide radical reactions with a number of the reduced sulfur compounds. Some of these reactions are considered to be important in boundary layer chemistry affecting tropospheric polar ozone. Further mechanistic information can be obtained from other reviews such as Tyndall and Ravishankara [1596].

Metal Chemistry

New results indicate that the Na + O_3 reaction produces NaO in the first excited electronic state. This observation may help explain the apparent low yield in laboratory studies of Na D-line emission from the NaO + O reaction, if the excited NaO lives long enough to react with O.

Sodium is deposited in the upper atmosphere by meteors along with larger amounts of silicon, magnesium, and iron; comparable amounts of aluminum, nickel, and calcium; and smaller amounts of potassium, chromium, manganese, and other elements. The interest is greatest in the alkali metals because they form the least stable oxides and thus free atoms can be regenerated through photolysis and reactions with O and O_3. The other meteoric elements are expected to form more stable oxides. A review by Plane [1991 #1062] describes many aspects of atmospheric metal chemistry.

The total flux of alkali metals through the atmosphere is relatively small, e.g., one or two orders of magnitude less than CFCs. Therefore extremely efficient catalytic cycles are required in order for Na to have a significant effect on stratospheric chemistry. There are no measurements of metals or metal compounds in the stratosphere which indicate a significant role.

It has been proposed that the highly polar metal compounds may polymerize to form clusters and that the stratospheric concentrations of free metal compounds are too small to play a significant role in the chemistry.

Some studies have shown that the polar species NaO and NaOH associate with abundant gases such as O_2 and CO_2 with very fast rates in the atmosphere. It has been proposed that reactions of this type will lead to the production of clusters with many molecules attached to the sodium

compounds. In most cases thermal dissociation is slow, and photolysis competes with the association reactions and limits the cluster concentrations in daylight. If atmospheric sodium does form large clusters, it is unlikely that Na species can have a significant role in stratospheric ozone chemistry. In order to assess the importance of these processes, data are needed on the association rates and the photolysis rates involving the cluster species.

Photochemical Data

There are new entries for HOBr and $CH_3C(O)O_2NO_2$ (PAN, peroxyacetyl nitrate) and significant new work has been published on the O_2 Herzberg continuum, ClOOCl, Cl_2O_3 and $BrONO_2$. Recent work on ClOOCl has suggested that cross sections in the long-wavelength tail where most of the photolysis occurs in the lower stratosphere may be significantly smaller than previously thought. Spectral artifacts arising from trace impurities are especially difficult to identify in this system leading to large uncertainties in the cross sections in this spectral region. The situation is similar for HOBr where a photodissociation study and one spectroscopic study indicate the presence of absorption features extending well into the visible region but other spectroscopic studies see no absorption beyond 400 nm.

Heterogeneous Chemistry

There is no question that heterogeneous processes on the surfaces of polar stratospheric cloud particles play a critical role in the chemistry of the winter and spring polar stratospheres. Furthermore, there is a great deal of observational and modeling evidence that heterogeneous reactions on background sulfuric acid aerosols play a very important role in stratospheric processes at both polar and mid-latitudes, particularly when stratospheric sulfate levels are elevated by major volcanic eruptions.

Polar heterogeneous chemical processes identified to date have a tendency to enhance the destruction of stratospheric ozone, primarily by converting relatively inactive "reservoir" species HCl and $ClONO_2$ to more active Cl_2 and HOCl, which are easily photolyzed to Cl and ClO. In some scenarios the heterogeneous reaction of HOCl and N_2O_5 with HCl may also play an important role in promoting the production of more easily photolyzed species. In addition, interaction with PSC surfaces can remove N_2O_5 and HNO_3 vapor from the polar stratosphere, sequestering nitrogen oxides in the form of condensed phase nitric acid and, thus, reducing the normal mitigating effect gaseous NO_x can have on ClO_x-catalyzed ozone destruction. The net effect of these processes is a major buildup of ClO_x radicals in PSC-processed polar stratospheric air masses and, particularly over the Antarctic, a massive springtime destruction of stratospheric ozone.

The reaction of stratospheric N_2O_5 with liquid water in sulfuric acid aerosols to form HNO_3 can have a significant impact on NO_x/HNO_3 ratios in the lower mid-latitude stratosphere, bringing measured mid-latitude ozone losses into better agreement with observations. Models suggest that at current mid-latitude ratios of NO_x/ClO_x this process increases ozone loss by lowering NO_x levels and thus reducing the scavenging of ClO by $ClONO_2$ formation. The reactions of $ClONO_2$ and $BrONO_2$ with sulfuric acid aerosol may also play a role in denitrification, the release of photolyzable halogen species, and the perturbation of HO_x radical levels.

The stratosphere also contains carbonaceous soot from aircraft and rocket exhausts, alumina and other metal oxides from solid propellant rocket exhaust and spacecraft debris, and, possibly, sodium chloride from some volcanic eruptions. There is increasing interest in determining if and when heterogeneous processes on these relatively minor surfaces can influence stratospheric chemistry.

Heterogeneous processes involving the liquid water droplets and ice crystals found in tropospheric clouds and aircraft contrails and/or the sulfate aerosols found in the free troposphere may have a significant effect on the flux into the stratosphere of reactive species from partially oxidized hydrohalocarbons or aircraft exhaust. Proper modeling of these processes will be necessary to assess the atmospheric impact of reducing the use of partially chlorinated hydrocarbon solvents, replacing CFCs with HCFCs and HFCs, and the evolution of the civil aviation industry.

The laboratory study of heterogeneous processes relevant to the stratosphere is an immature field in comparison to the measurement of gas phase kinetic and photodissociation parameters. Heterogeneous experimental techniques are not yet as well developed and the interpretation of experimental data is significantly more complex. Nonetheless, over the past several years, a number of experimental groups have made very significant progress and data from complementary techniques are increasingly available to help determine when the quantification of heterogeneous kinetic processes has been successfully distinguished from complicating mass transport and surface saturation processes.

However, it is well to remember that quantitative application of laboratory results on heterogeneous processes to the stratosphere is not straightforward. First, there is still a significant level of uncertainty in both the detailed chemical and physical characteristics of the droplet and particle surfaces present in the stratosphere and in how faithful the laboratory simulation of these surfaces in various experimental configurations may be. Secondly, the proper incorporation of heterogeneous processes into models of stratospheric and upper tropospheric chemistry is very difficult and no current models incorporate formation of and reaction on droplet/particle surfaces in a fully coupled and self-consistent way. A great deal of effort will have to be expended before the modeling community is as adept at incorporating heterogeneous effects as they are in representing gas phase kinetic and photochemical processes.

TABLE 1. Rate Constants for Second Order Reactions

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
O_x Reactions					
$O + O_2 \xrightarrow{M} O_3$	(See Table 2)				
$O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-12}	2060±250	8.0×10^{-15}	1.15	A1
$O(^1D)$ Reactions					
$O(^1D) + O_2 \rightarrow O + O_2$	3.2×10^{-11}	-(70±100)	4.0×10^{-11}	1.2	A2,A3
$O(^1D) + O_3 \rightarrow O_2 + O_2$	1.2×10^{-10}	0±100	1.2×10^{-10}	1.3	A2, A4
$\rightarrow O_2 + O + O$	1.2×10^{-10}	0±100	1.2×10^{-10}	1.3	A2, A4
$O(^1D) + H_2 \rightarrow OH + H$	[illegible]				
$O(^1D) + H_2O \rightarrow OH + OH$	2.2×10^{-10}	0±100	2.2×10^{-10}	1.2	A2
$O(^1D) + N_2 \rightarrow O + N_2$	1.8×10^{-11}	-(110±100)	2.6×10^{-11}	1.2	A2
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(See Table 2)				
$O(^1D) + N_2O \rightarrow N_2 + O_2$	4.9×10^{-11}	0±100	4.9×10^{-11}	1.3	A2, A7
$\rightarrow NO + NO$	6.7×10^{-11}	0±100	6.7×10^{-11}	1.3	A2, A7
$O(^1D) + NH_3 \rightarrow OH + NH_2$	2.5×10^{-10}	0±100	2.5×10^{-10}	1.3	A2, A8
$O(^1D) + CO_2 \rightarrow O + CO_2$	7.4×10^{-11}	-(120±100)	1.1×10^{-10}	1.2	A2
$O(^1D) + CH_4 \rightarrow$ products	1.5×10^{-10}	0±100	1.5×10^{-10}	1.2	A2 [illegible]
$O(^1D) + HCl \rightarrow$ products	1.5×10^{-10}	0±100	1.5×10^{-10}	1.2	[illegible]
$O(^1D) + HF \rightarrow OH + F$	1.4×10^{-10}	0±100	1.4×10^{-10}	2.0	A11
$O(^1D) + HBr \rightarrow$ products	1.5×10^{-10}	0±100	1.5×10^{-10}	2.0	A12
$O(^1D) + Cl_2 \rightarrow$ products	2.8×10^{-10}	0±100	2.8×10^{-10}	2.0	[illegible]
$O(^1D) + CCl_2O \rightarrow$ products	3.6×10^{-10}	0±100	3.6×10^{-10}	2.0	A2, A14
$O(^1D) + CClFO \rightarrow$ products	1.9×10^{-10}	0±100	1.9×10^{-10}	2.0	A2, A14
$O(^1D) + CF_2O \rightarrow$ products	7.4×10^{-11}	0±100	7.4×10^{-11}	2.0	A2, A14

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$O(^1D) + CCl_4 \rightarrow$ products (CFC-10)	$3.3x10^{-10}$	0±100	$3.3x10^{-10}$	1.2	A2, A15
$O(^1D) + CH_3Br \rightarrow$ products	$1.8x10^{-10}$	0±100	$1.8x10^{-10}$	1.3	A15, A16
$O(^1D) + CH_2Br_2 \rightarrow$ products	$2.7x10^{-10}$	0±100	$2.7x10^{-10}$	1.3	A15, A17
$O(^1D) + CHBr_3 \rightarrow$ products	$6.6x10^{-10}$	0±100	$6.6x10^{-10}$	1.5	A15, A18
$O(^1D) + CH_3F \rightarrow$ products (HFC-41)	$1.5x10^{-10}$	0±100	$1.5x10^{-10}$	1.2	A15 A19
$O(^1D) + CH_2F_2 \rightarrow$ products (HFC-32)	$5.1x10^{-11}$	0±100	$5.1x10^{-11}$	1.3	A15, A20
$O(^1D) + CHF_3 \rightarrow$ products (HFC-23)	$9.1x10^{-12}$	0±100	$9.1x10^{-12}$	1.2	A15, A21
$O(^1D) + CHCl_2F \rightarrow$ products (HCFC-21)	$1.9x10^{-10}$	0±100	$1.9x10^{-10}$	1.3	A15 A22
$O(^1D) + CHClF_2 \rightarrow$ products (HCFC-22)	$1.0x10^{-10}$	0±100	$1.0x10^{-10}$	1.2	A15,A23
$O(^1D) + CCl_3F \rightarrow$ products (CFC-11)	$2.3x10^{-10}$	0±100	$2.3x10^{-10}$	1.2	A2 A15
$O(^1D) + CCl_2F_2 \rightarrow$ products (CFC-12)	$1.4x10^{-10}$	0±100	$1.4x10^{-10}$	1.3	A2 A15
$O(^1D) + CClF_3 \rightarrow$ products (CFC-13)	$8.7x10^{-11}$	0±100	$8.7x10^{-11}$	1.3	A15 A24
$O(^1D) + CClBrF_2 \rightarrow$ products (Halon-1211)	$1.5x10^{-10}$	0±100	$1.5x10^{-10}$	1.3	A15,A25
$O(^1D) + CBr_2F_2 \rightarrow$ products (Halon-1202)	$2.2x10^{-10}$	0±100	$2.2x10^{-10}$	1.3	A15,A26
$O(^1D) + CBrF_3 \rightarrow$ products (Halon-1301)	$1.0x10^{-10}$	0±100	$1.0x10^{-10}$	1.3	A15 A27
$O(^1D) + CF_4 \rightarrow CF_4 + O$ (CFC-14)	-	-	$2.0x10^{-14}$	1.5	A15,A28
$O(^1D) + CH_3CH_2F \rightarrow$ products (HFC-161)	$2.6x10^{-10}$	0±100	$2.6x10^{-10}$	1.3	A15,A29

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$O(^1D) + CH_3CHF_2 \rightarrow$ products (HFC-152a)	2.0×10^{-10}	0±100	2.0×10^{-10}	1.3	A15,A30
$O(^1D) + CH_3CCl_2F \rightarrow$ products (HCFC-141b)	2.6×10^{-10}	0±100	2.6×10^{-10}	1.3	A15,A31
$O(^1D) + CH_3CClF_2 \rightarrow$ products (HCFC-142b)	2.2×10^{-10}	0±100	2.2×10^{-10}	1.3	A15,A32
$O(^1D) + CH_3CF_3 \rightarrow$ products (HFC-143a)	1.0×10^{-10}	0±100	1.0×10^{-10}	3.0	A15,A33
$O(^1D) + CH_2ClCClF_2 \rightarrow$ products (HCFC-132b)	1.6×10^{-10}	0±100	1.6×10^{-10}	2.0	A15,A34
$O(^1D) + CH_2ClCF_3 \rightarrow$ products (HCFC-133a)	1.2×10^{-10}	0±100	1.2×10^{-10}	1.3	A15,A35
$O(^1D) + CH_2FCF_3 \rightarrow$ products (HFC-134a)	4.9×10^{-11}	0±100	4.9×10^{-11}	1.3	A15,A36
$O(^1D) + CHCl_2CF_3 \rightarrow$ products (HCFC-123)	2.0×10^{-10}	0±100	2.0×10^{-10}	1.3	A15,A37
$O(^1D) + CHClFCF_3 \rightarrow$ products (HCFC-124)	8.6×10^{-11}	0±100	8.6×10^{-11}	1.3	A15,A38
$O(^1D) + CHF_2CF_3 \rightarrow$ products (HCFC-125)	1.2×10^{-10}	0±100	1.2×10^{-10}	2.0	A15,A39
$O(^1D) + CCl_3CF_3 \rightarrow$ products (CFC-113a)	2×10^{-10}	0±100	2×10^{-10}	2.0	A15,A40
$O(^1D) + CCl_2FCClF_2 \rightarrow$ products (CFC-113)	2×10^{-10}	0±100	2×10^{-10}	2.0	A15,A41
$O(^1D) + CCl_2FCF_3 \rightarrow$ products (CFC-114a)	1×10^{-10}	0±100	1×10^{-10}	2.0	A15,A42
$O(^1D) + CClF_2CClF_2 \rightarrow$ products (CFC-114)	1.3×10^{-10}	0±100	1.3×10^{-10}	1.3	A15,A43
$O(^1D) + CClF_2CF_3 \rightarrow$ products (CFC-115)	5×10^{-11}	0±100	5×10^{-11}	1.3	A15,A44
$O(^1D) + CBrF_2CBrF_2 \rightarrow$ products (Halon-2402)	1.6×10^{-10}	0±100	1.6×10^{-10}	1.3	A15

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$O(^1D) + CF_3CF_3 \rightarrow O + CF_3CF_3$ (CFC-116)	-	-	$1.5x10^{-13}$	1.5	A15,A46
$O(^1D) + CHF_2CF_2CF_2CHF_2 \rightarrow$ products (HFC-338pcc)	$1.8x10^{-11}$	0±100	$1.8x10^{-11}$	1.5	A15,A47
$O(^1D) + c\text{-}C_4F_8 \rightarrow$ products	-	-	$8x10^{-13}$	1.3	A15,A48
$O(^1D) + CF_3CHFCHFCF_2CF_3 \rightarrow$ products (HFC-43-10mee)	$2.1x10^{-10}$	0±100	$2.1x10^{-10}$	4	A15,A49
$O(^1D) + C_5F_{12} \rightarrow$ products (CFC-41-12)	-	-	$3.9x10^{-13}$	2	A15,A50
$O(^1D) + C_6F_{14} \rightarrow$ products (CFC-51-14)	-	-	$1x10^{-12}$	2	A15,A51
$O(^1D) + 1,2\text{-}(CF_3)_2c\text{-}C_4F_6 \rightarrow$ products	-	-	$2.8x10^{-13}$	2	A15,A52
$O(^1D) + SF_6 \rightarrow$ products	-	-	$1.8x10^{-14}$	1.5	A53
<u>Singlet O_2 Reactions</u>					
$O_2(^1\Delta) + O \rightarrow$ products	-	-	$<2x10^{-16}$	-	A54
$O_2(^1\Delta) + O_2 \rightarrow$ products	$3.6x10^{-18}$	220±100	$1.7x10^{-18}$	1.2	A55
$O_2(^1\Delta) + O_3 \rightarrow O + 2O_2$	$5.2x10^{-11}$	2840±500	$3.8x10^{-15}$	1.2	A56
$O_2(^1\Delta) + H_2O \rightarrow$ products	-	-	$4.8x10^{-18}$	1.5	A57
$O_2(^1\Delta) + N \rightarrow NO + O$	-	-	$<9x10^{-17}$	-	A58
$O_2(^1\Delta) + N_2 \rightarrow$ products	-	-	$<10^{-20}$	-	A59
$O_2(^1\Delta) + CO_2 \rightarrow$ products	-	-	$<2x10^{-20}$	-	A60
$O_2(^1\Sigma) + O \rightarrow$ products	-	-	$8x10^{-14}$	5.0	A61
$O_2(^1\Sigma) + O_2 \rightarrow$ products	-	-	$3.9x10^{-17}$	1.5	A62
$O_2(^1\Sigma) + O_3 \rightarrow$ products	$2.2x10^{-11}$	0±200	$2.2x10^{-11}$	1.2	A63
$O_2(^1\Sigma) + H_2O \rightarrow$ products	-	-	$5.4x10^{-12}$	1.3	A64
$O_2(^1\Sigma) + N \rightarrow$ products	-	-	$<10^{-13}$	-	A65

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$O_2(^1\Sigma) + N_2 \rightarrow$ products	2.1×10^{-15}	0±200	2.1×10^{-15}	1.2	A66
$O_2(^1\Sigma) + CO_2 \rightarrow$ products	4.2×10^{-13}	0±200	4.2×10^{-13}	1.2	A67
<u>HO_x Reactions</u>					
$O + OH \rightarrow O_2 + H$	2.2×10^{-11}	-(120±100)	3.3×10^{-11}	1.2	B 1
$O + HO_2 \rightarrow OH + O_2$	3.0×10^{-11}	-(200±100)	5.9×10^{-11}	1.2	B 2
$O + H_2O_2 \rightarrow OH + HO_2$	1.4×10^{-12}	2000±1000	1.7×10^{-15}	2.0	B 3
$H + O_2 \xrightarrow{M} HO_2$	(See Table 2)				
$H + O_3 \rightarrow OH + O_2$	1.4×10^{-10}	470±200	2.9×10^{-11}	1.25	B 4
$H + HO_2 \rightarrow$ products	8.1×10^{-11}	0±100	8.1×10^{-11}	1.3	B 5
$OH + O_3 \rightarrow HO_2 + O_2$	1.6×10^{-12}	940±300	6.8×10^{-14}	1.3	B 6
$OH + H_2 \rightarrow H_2O + H$	5.5×10^{-12}		6.7×10^{-15}		
$OH + HD \rightarrow$ products			4.0×10^{-15}		
$OH + OH \rightarrow H_2O + O$	4.2×10^{-12}	240±240	1.9×10^{-12}	1.4	B 9
$\xrightarrow{M} H_2O_2$	(See Table 2)				
$OH + HO_2 \rightarrow H_2O + O_2$	4.8×10^{-11}	-(250±200)	1.1×10^{-10}	1.3	B10
$OH + H_2O_2 \rightarrow H_2O + HO_2$	2.9×10^{-12}	160±100	1.7×10^{-12}	1.2	B11
$HO_2 + O_3 \rightarrow OH + 2O_2$	1.1×10^{-14}	$500\pm\frac{500}{100}$	2.0×10^{-15}	1.3	B12
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.3×10^{-13}	-(600±200)	1.7×10^{-12}	1.3	B13
$\xrightarrow{M} H_2O_2 + O_2$	1.7×10^{-33}[M]	-(1000±400)	4.9×10^{-32}[M]	1.3	B13
<u>NO_x Reactions</u>					
$O + NO \xrightarrow{M} NO_2$	(See Table 2)				
$O + NO_2 \rightarrow NO + O_2$	6.5×10^{-12}	-(120±120)	9.7×10^{-12}	1.1	C 1
$O + NO_2 \xrightarrow{M} NO_3$	(See Table 2)				
$O + NO_3 \rightarrow O_2 + NO_2$	1.0×10^{-11}	0±150	1.0×10^{-11}	1.5	C 2
$O + N_2O_5 \rightarrow$ products			$<3.0\times10^{-16}$		C 3

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$O + HNO_3 \rightarrow OH + NO_3$			$<3.0\times10^{-17}$		C 4
$O + HO_2NO_2 \rightarrow$ products	7.8×10^{-11}	3400±750	8.6×10^{-16}	3.0	C 5
$H + NO_2 \rightarrow OH + NO$	4.0×10^{-10}	340±300	1.3×10^{-10}	1.3	C 6
$OH + NO \xrightarrow{M} HONO$	(See Table 2)				
$OH + NO_2 \xrightarrow{M} HNO_3$	(See Table 2)				
$OH + NO_3 \rightarrow$ products			2.2×10^{-11}	1.5	C 7
$OH + HONO \rightarrow H_2O + NO_2$	1.8×10^{-11}	$390\pm^{200}_{500}$	4.5×10^{-12}	1.5	C 8
$OH + HNO_3 \rightarrow H_2O + NO_3$	(See Note)			1.3	C 9
$OH + HO_2NO_2 \rightarrow$ products	1.3×10^{-12}	$-(380\pm^{270}_{500})$	4.6×10^{-12}	1.5	C10
$OH + NH_3 \rightarrow H_2O + NH_2$	1.7×10^{-12}	710±200	1.6×10^{-13}	1.2	C11
$HO_2 + NO \rightarrow NO_2 + OH$	3.5×10^{-12}	-(250±100)	8.5×10^{-12}	1.15	C12
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(See Table 2)				
$HO_2 + NO_2 \rightarrow HONO + O_2$	(See Note)				C13
$HO_2 + NO_3 \rightarrow$ products			3.5×10^{-12}	1.5	C14
$HO_2 + NH_2 \rightarrow$ products			3.4×10^{-11}	2.0	C15
$N + O_2 \rightarrow NO + O$	1.5×10^{-11}	3600±400	8.5×10^{-17}	1.25	C16
$N + O_3 \rightarrow NO + O_2$			$<2.0\times10^{-16}$		C17
$N + NO \rightarrow N_2 + O$	2.1×10^{-11}	-(100±100)	3.0×10^{-11}	1.3	C18
$N + NO_2 \rightarrow N_2O + O$	5.8×10^{-12}	-(220±100)	1.2×10^{-11}	1.5	C19
$NO + O_3 \rightarrow NO_2 + O_2$	2.0×10^{-12}	1400±200	1.8×10^{-14}	1.1	C20
$NO + NO_3 \rightarrow 2NO_2$	1.5×10^{-11}	-(170±100)	2.6×10^{-11}	1.3	C21
$NO_2 + O_3 \rightarrow NO_3 + O_2$	1.2×10^{-13}	2450±150	3.2×10^{-17}	1.15	C22
$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	(See Note)				C23

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(See Table 2)				
$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$	8.5×10^{-13}	2450±500	2.3×10^{-16}	1.5	C24
$NH_2 + O_2 \rightarrow$ products			$<6.0\times10^{-21}$		C25
$NH_2 + O_3 \rightarrow$ products	4.3×10^{-12}	930±500	1.9×10^{-13}	3.0	C26
$NH_2 + NO \rightarrow$ products	[redacted]	-(450±150)	[redacted]		C27
$NH_2 + NO_2 \rightarrow$ products	2.1×10^{-12}	-(650±250)	1.9×10^{-11}	3.0	C28
$NH + NO \rightarrow$ products	4.9×10^{-11}	0±300	4.9×10^{-11}	1.5	C29
$NH + NO_2 \rightarrow$ products	3.5×10^{-13}	-(1140±500)	1.6×10^{-11}	2.0	C30
$O_3 + HNO_2 \rightarrow O_2 + HNO_3$			$<5.0\times10^{-19}$		C31
$N_2O_5 + H_2O \rightarrow 2HNO_3$			$<2.0\times10^{-21}$		C32
$N_2(A,v) + O_2 \rightarrow$ products			2.5×10^{-12}, v=0	1.5	C33
$N_2(A,v) + O_3 \rightarrow$ products			4.1×10^{-11}, v=0	2.0	C34
Hydrocarbon Reactions					
$O + CH_3 \rightarrow$ products	1.1×10^{-10}	0±250	1.1×10^{-10}	1.3	D1
$O + HCN \rightarrow$ products	1.0×10^{-11}	4000±1000	1.5×10^{-17}	10	D2
$O + C_2H_2 \rightarrow$ products	3.0×10^{-11}	1600±250	1.4×10^{-13}	1.3	D3
$O + H_2CO \rightarrow$ products	3.4×10^{-11}	1600±250	1.6×10^{-13}	1.25	D4
$O + CH_3CHO \rightarrow CH_3CO + OH$	1.8×10^{-11}	1100±200	4.5×10^{-13}	1.25	D5
$O_3 + C_2H_2 \rightarrow$ products	1.0×10^{-14}	4100±500	1.0×10^{-20}	3	D6
$O_3 + C_2H_4 \rightarrow$ products	1.2×10^{-14}	2630±100	1.7×10^{-18}	1.25	D7
$O_3 + C_3H_6 \rightarrow$ products	6.5×10^{-15}	1900±200	1.1×10^{-17}	1.2	D8
$OH + CO \rightarrow$ Products	1.5×10^{-13} x $(1+0.6P_{atm})$	0±300	1.5×10^{-13} x $(1+0.6P_{atm})$	1.3	[redacted]
$OH + CH_4 \rightarrow CH_3 + H_2O$	[redacted]			1.1	
$OH + {}^{13}CH_4 \rightarrow {}^{13}CH_3 + H_2O$	(See Note)				D11
$OH + CH_3D \rightarrow$ products	3.5×10^{-12}	1950 ± 200	5.0×10^{-15}	1.15	D12

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$OH + H_2CO \rightarrow H_2O + HCO$	$1.0x10^{-11}$	0±200	$1.0x10^{-11}$	1.25	D13
$OH + CH_3OH \rightarrow$ products	$6.7x10^{-12}$	600±300	$8.9x10^{-13}$	1.2	D14
$OH + CH_3OOH \rightarrow$ Products	$3.8x10^{-12}$	-(200±200)	$7.4x10^{-12}$	1.5	D15
$OH + HC(O)OH \rightarrow$ products	$4.0x10^{-13}$	0±200	$4.0x10^{-13}$	1.3	D16
$OH + HCN \rightarrow$ products	$1.2x10^{-13}$	400±150	$3.1x10^{-14}$	3	D17
$OH + C_2H_2 \xrightarrow{M}$ products	(See Table 2)				
$OH + C_2H_4 \xrightarrow{M}$ products	(See Table 2)				
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	8.7×10^{-12}	1070±100	$2.4x10^{-13}$	1.1	D18
$OH + C_3H_8 \rightarrow H_2O + C_3H_7$	1.0×10^{-11}	660±100	$1.1x10^{-12}$	1.2	D19
$OH + CH_3CHO \rightarrow CH_3CO + H_2O$	$5.6x10^{-12}$	-(270±200)	$1.4x10^{-11}$	1.2	D20
$OH + C_2H_5OH \rightarrow$ products	$7.0x10^{-12}$	235±100	$3.2x10^{-12}$	1.3	D21
$OH + CH_3C(O)OH \rightarrow$ products	$4.0x10^{-13}$	-200±400	$8.0x10^{-13}$	1.3	D22
$OH + CH_3C(O)CH_3 \rightarrow CH_3C(O)CH_2 + H_2O$	2.2×10^{-12}	685±100	$2.2x10^{-13}$	1.15	D23
$OH + CH_3CN \rightarrow$ products	$7.8x10^{-13}$	1050±200	$2.3x10^{-14}$	1.5	D24
$OH + CH_3ONO_2 \rightarrow$ products	$5.0x10^{-13}$	890±100	$2.4x10^{-14}$	3	D25
$OH + CH_3C(O)O_2NO_2$ (PAN)$\rightarrow$ products			$<4 \times 10^{-14}$		D26
$OH + C_2H_5ONO_2 \rightarrow$ products	$8.2x10^{-13}$	450±100	$1.8x10^{-13}$	3	D27
$HO_2 + CH_2O \rightarrow$ adduct	$6.7x10^{-15}$	-(600±600)	$5.0x10^{-14}$	5	D28
$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$	$3.8x10^{-13}$	-(800±400)	$5.6x10^{-12}$	2	D29
$HO_2 + C_2H_5O_2 \rightarrow C_2H_5OOH + O_2$	$7.5x10^{-13}$	-(700±250)	$8.0x10^{-12}$	1.5	D30
$HO_2 + CH_3C(O)O_2 \rightarrow$ products	$4.5x10^{-13}$	-(1000±600)	$1.3x10^{-11}$	2	D31
$NO_3 + CO \rightarrow$ products			$<4.0x10^{-19}$		D32
$NO_3 + CH_2O \rightarrow$ products			$5.8x10^{-16}$	1.3	D33
$NO_3 + CH_3CHO \rightarrow$ products	$1.4x10^{-12}$	1900±300	$2.4x10^{-15}$	1.3	D34
$CH_3 + O_2 \rightarrow$ products			$<3.0x10^{-16}$		D35
$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(See Table 2)				
$CH_3 + O_3 \rightarrow$ products	$5.4x10^{-12}$	220±150	$2.6x10^{-12}$	2	D36

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$HCO + O_2 \rightarrow CO + HO_2$	$3.5x10^{-12}$	-(140±140)	$5.5x10^{-12}$	1.3	D37
$CH_2OH + O_2 \rightarrow CH_2O + HO_2$			$9.1x10^{-12}$	1.3	D38
$CH_3O + O_2 \rightarrow CH_2O + HO_2$	$3.9x10^{-14}$	900±300	$1.9x10^{-15}$	1.5	D39
$CH_3O + NO \rightarrow CH_2O + HNO$	(See Note)				D40
$CH_3O + NO \xrightarrow{M} CH_3ONO$	(See Table 2)				
$CH_3O + NO_2 \xrightarrow{M} CH_3ONO_2$	(See Table 2)				
$CH_3O + NO_2 \rightarrow CH_2O + HONO$	$1.1 x 10^{-11}$	[illegible]	$2.0 x 10^{-13}$	5	D41
$CH_3O_2 + O_3 \rightarrow$ products			$<3.0x10^{-17}$		D42
$CH_3O_2 + CH_3O_2 \rightarrow$ products	$2.5x10^{-13}$	-(190±190)	$4.7x10^{-13}$	1.5	D43
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	$4.2x10^{-12}$	-(180±180)	$7.7x10^{-12}$	1.5	D44
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(See Table 2)				
$CH_3O_2 + CH_3C(O)O_2 \rightarrow$ products	[illegible]			1.5	D45
$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$			$<2.0x10^{-14}$		D46
$C_2H_5 + O_2 \xrightarrow{M} C_2H_5O_2$	(See Table 2)				
$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	6.3×10^{-14}	550±200	$1.0x10^{-14}$	1.5	D47
$C_2H_5O + NO \xrightarrow{M}$ products	(See Table 2)				
$C_2H_5O + NO_2 \xrightarrow{M}$ products	(See Table 2)				
$C_2H_5O_2 + C_2H_5O_2 \rightarrow$ products	$6.8x10^{-14}$	0±300	$6.8x10^{-14}$	2	D48
$C_2H_5O_2 + NO \rightarrow$ products	[illegible]			1.2	D49
$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow$ products				1.3	D50
$CH_3C(O)O_2 + NO \rightarrow$ products				1.4	D51
$CH_3C(O)O_2 + NO_2 \xrightarrow{M}$ products	(See Table 2)				
FO_x Reactions					
$O + FO \rightarrow F + O_2$	$2.7x10^{-11}$	0±250	$2.7x10^{-11}$	3.0	E 1
$O + FO_2 \rightarrow FO + O_2$	$5.0x10^{-11}$	0±250	$5.0x10^{-11}$	5.0	E 2
$OH + CH_3F \rightarrow CH_2F + H_2O$ (HFC-41)	$3.0x10^{-12}$	1500±300	$2.0x10^{-14}$	1.1	E 3

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$OH + CH_2F_2 \rightarrow CHF_2 + H_2O$ (HFC-32)	$1.9x10^{-12}$	1550±200	$1.0x10^{-14}$	1.2	E 4
$OH + CHF_3 \rightarrow CF_3 + H_2O$ (HFC-23)	$1.0x10^{-12}$	2440±200	$2.8x10^{-16}$	1.4	E 5
$OH + CF_3OH \rightarrow CF_3O + H_2O$			$<2x10^{-17}$		E6
$OH + CH_3CH_2F \rightarrow$ products (HFC-161)	$7.0x10^{-12}$	1100±300	$1.7x10^{-13}$	1.4	E 7
$OH + CH_3CHF_2 \rightarrow$ products (HFC-152a)	$2.4x10^{-12}$	1260±200	$3.5x10^{-14}$	1.2	E 8
$OH + CH_2FCH_2F \rightarrow CHFCH_2F + H_2O$ (HFC-152)	$1.7x10^{-11}$	1500±500	$1.1x10^{-13}$	2.0	E 9
$OH + CH_3CF_3 \rightarrow CH_2CF_3 + H_2O$ (HFC-143a)	$1.8x10^{-12}$	2170±150	$1.2x10^{-15}$	1.1	E 10
$OH + CH_2FCHF_2 \rightarrow$ products (HFC-143)	$4.0x10^{-12}$	1650±300	$1.6x10^{-14}$	1.5	E11
$OH + CH_2FCF_3 \rightarrow CHFCF_3 + H_2O$ (HFC-134a)	$1.5x10^{-12}$	1750±200	$4.2x10^{-15}$	1.1	E12
$OH + CHF_2CHF_2 \rightarrow CF_2CHF_2 + H_2O$ (HFC-134)	$1.6x10^{-12}$	1680±300	$5.7x10^{-15}$	2.0	E13
$OH + CHF_2CF_3 \rightarrow CF_2CF_3 + H_2O$ (HFC-125)	$5.6x10^{-13}$	1700±300	$1.9x10^{-15}$	1.3	E14
$OH + CH_3OCHF_2 \rightarrow$ products (HFOC-152a)	$2.0x10^{-12}$	1200±300	$1.2x10^{-14}$	1.5	E15
$OH + CF_3OCH_3 \rightarrow CF_3OCH_2 + H_2O$ (HFOC-143a)	$1.5x10^{-12}$	1800±300	$3.5x10^{-15}$	1.2	E16
$OH + CF_2HOCF_2H \rightarrow CF_2OCF_2H + H_2O$ (HFOC-134)	$1.1x10^{-12}$	1200±300	$1.2x10^{-14}$	1.5	E17
$OH + CF_3OCHF_2 \rightarrow CF_3OCF_2 + H_2O$ (HFOC-125)	$4.7x10^{-13}$	2100±300	$4.1x10^{-16}$	1.2	E18
$OH + CF_3CH_2CH_3 \rightarrow$ products (HFC-263fb)	$1.3x10^{-12}$	1000±300	$2.1x10^{-14}$	1.5	E19
$OH + CH_2FCF_2CHF_2 \rightarrow$ products (HFC-245ca)	$2.4x10^{-12}$	1660±150	$9.1x10^{-15}$	1.3	E20
$OH + CHF_2CHFCHF_2 \rightarrow$ products (HFC-245ea)	$1.4x10^{-12}$	1200±300	$1.6x10^{-14}$	1.5	E21

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
OH + CF_3CHFCH_2F → products (HFC-245eb)	-	-	$1.5x10^{-14}$	2.0	E22
OH + $CHF_2CH_2CF_3$ → products (HFC-245fa)	$6.1x10^{-13}$	1330±150	$7.0x10^{-15}$	1.2	E23
OH + $CF_3CF_2CH_2F$ → CF_3CF_2CHF + H_2O (HFC-236cb)	$1.5x10^{-12}$	1750±500	$4.2x10^{-15}$	2.0	E24
OH + $CF_3CHFCHF_2$ → products (HFC-236ea)	$1.1x10^{-12}$	1590±150	$5.3x10^{-15}$	1.1	E25
OH + $CF_3CH_2CF_3$ → CF_3CHCF_3 + H_2O (HFC-236fa)	$1.3x10^{-12}$	2480±150	$3.2x10^{-16}$	1.1	E26
OH + CF_3CHFCF_3 → CF_3CFCF_3+H_2O (HFC-227ea)	$5.0x10^{-13}$	1700±300	$1.7x10^{-15}$	1.1	E27
OH + $CHF_2OCH_2CF_3$ → products (HFOC-245fa)	$2.6x10^{-12}$	1410±150	$1.2x10^{-14}$	1.2	E28
OH + $CF_3CH_2CF_2CH_3$ → products (HFC-365mfc)	$3.0x10^{-12}$	1710±200	$5.7x10^{-15}$	1.3	E29
OH + $CF_3CH_2CH_2CF_3$ → products (HFC-356mff)	$3.0x10^{-12}$	1800±500	$7.1x10^{-15}$	1.3	E30
OH + $CF_3CF_2CH_2CH_2F$ → products (HFC-356mcf)	$1.5x10^{-12}$	1110±200	$4.2x10^{-14}$	2.0	E31
OH + $CHF_2CF_2CF_2CF_2H$ → products (HFC-338pcc)	$7.8x10^{-13}$	1530±200	$4.6x10^{-15}$	1.5	E32
OH + $CF_3CH_2CF_2CF_3$ → products (HFC-43-10mef)	$5.2x10^{-13}$	1500±300	$3.4x10^{-15}$	1.3	E33
OH + $CF_3CHFCHFCF_2CF_3$ → products (HFC-43-10mee)	$5.2x10^{-13}$	1500±300	$3.4x10^{-15}$	1.3	E34
OH + $CF_3CF_2CF_2CF_2CF_3$ → products (HFC-43-10mcf)	$1.4x10^{-12}$	1500±300	$8.3x10^{-15}$	1.5	E35
$F + O_2 \xrightarrow{M} FO_2$	(See Table 2)				
$F + O_3 \rightarrow FO + O_2$	$2.2x10^{-11}$	230±200	$1.0x10^{-11}$	1.5	E36
$F + H_2 \rightarrow HF + H$	$1.4x10^{-10}$	500±200	$2.6x10^{-11}$	1.2	E37
$F + H_2O \rightarrow HF + OH$	$1.4x10^{-11}$	0±200	$1.4x10^{-11}$	1.3	E38
$F + NO \xrightarrow{M} FNO$	(See Table 2)				

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$F + NO_2 \xrightarrow{M} FNO_2$	(See Table 2)				
$F + HNO_3 \rightarrow HF + NO_3$	6.0×10^{-12}	-(400±200)	2.3×10^{-11}	1.3	E39
$F + CH_4 \rightarrow HF + CH_3$	1.6×10^{-10}	260±200	6.7×10^{-11}	1.4	E40
$FO + O_3 \rightarrow$ products			$<1 \times 10^{-14}$		E41
$FO + NO \rightarrow NO_2 + F$	8.2×10^{-12}	-(300±200)	2.2×10^{-11}	1.5	E42
$FO + NO_2 \xrightarrow{M} FONO_2$	(See Table 2)				
$FO + FO \rightarrow 2\,F + O_2$	1.0×10^{-11}	0±250	1.0×10^{-11}	1.5	E43
$FO_2 + O_3 \rightarrow$ products			$<3.4 \times 10^{-16}$		E44
$FO_2 + NO \rightarrow FNO + O_2$	7.5×10^{-12}	690±400	7.5×10^{-13}	2.0	E45
$FO_2 + NO_2 \rightarrow$ products	3.8×10^{-11}	2040±500	4.0×10^{-14}	2.0	E46
$FO_2 + CO \rightarrow$ products			$<5.1 \times 10^{-16}$		E47
$FO_2 + CH_4 \rightarrow$ products			$<2 \times 10^{-16}$		E48
$CF_3 + O_2 \xrightarrow{M} CF_3O_2$	(See Table 2)				
$CF_3O + M \rightarrow F + CF_2O + M$	(See Table 2)				
$CF_3O + O_2 \rightarrow FO_2 + CF_2O$	$<3 \times 10^{-11}$	5000	$<1.5 \times 10^{-18}$		E49
$CF_3O + O_3 \rightarrow CF_3O_2 + O_2$	2×10^{-12}	1400±600	1.8×10^{-14}	1.3	E50
$CF_3O + H_2O \rightarrow OH + CF_3OH$	3×10^{-12}	>3600	$<2 \times 10^{-17}$		E51
$CF_3O + NO \rightarrow CF_2O + FNO$	3.7×10^{-11}	(-110±70)	5.4×10^{-11}	1.2	E52
$CF_3O + NO_2 \rightarrow$ products	(See Note)				E53
$\xrightarrow{M} CF_3ONO_2$	(See Table 2)				
$CF_3O + CO \rightarrow$ products			$<2 \times 10^{-15}$		E54
$\xrightarrow{M} CF_3OCO$	(See Table 2)				
$CF_3O + CH_4 \rightarrow CH_3 + CF_3OH$	2.6×10^{-12}	1420±200	2.2×10^{-14}	1.1	E55
$CF_3O + C_2H_6 \rightarrow C_2H_5 + CF_3OH$	4.9×10^{-12}	400±100	1.3×10^{-12}	1.2	E56
$CF_3O_2 + O_3 \rightarrow CF_3O + 2O_2$			$<3 \times 10^{-15}$		E57

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$CF_3O_2 + CO \rightarrow CF_3O + CO_2$			$<5 \times 10^{-16}$		E58
$CF_3O_2 + NO \rightarrow CF_3O + NO_2$	5.4×10^{-12}	(-320±150)	1.6×10^{-11}		
$CF_3O_2 + NO_2 \xrightarrow{M} CF_3O_2NO_2$	(See Table 2)				
<u>ClO_x Reactions</u>					
$O + ClO \rightarrow Cl + O_2$	3.0×10^{-11}	-(70±70)	3.8×10^{-11}	1.2	F 1
$O + OClO \rightarrow ClO + O_2$	2.4×10^{-12}	960±300	1.0×10^{-13}	2.0	F 2
$O + OClO \xrightarrow{M} ClO_3$	(See Table 2)				
$O + Cl_2O \rightarrow ClO + ClO$	2.7×10^{-11}	530±150	4.5×10^{-12}	1.3	F 3
$O + HCl \rightarrow OH + Cl$	1.0×10^{-11}	3300±350	1.5×10^{-16}	2.0	F 4
$O + HOCl \rightarrow OH + ClO$					
$O + ClONO_2 \rightarrow$ products	2.9×10^{-12}	800±200	2.0×10^{-13}	1.5	F 6
$O_3 + OClO \rightarrow$ products	2.1×10^{-12}	4700±1000	3.0×10^{-19}	2.5	F 7
$O_3 + Cl_2O_2 \rightarrow$ products	-	-	$<1.0 \times 10^{-19}$	-	F 8
$OH + Cl_2 \rightarrow HOCl + Cl$	1.4×10^{-12}	900±400	6.7×10^{-14}	1.2	F 9
$OH + ClO \rightarrow$ products	1.1×10^{-11}	-(120±150)	1.7×10^{-11}	1.5	F10
$OH + OClO \rightarrow HOCl + O_2$	4.5×10^{-13}	-(800±200)	6.8×10^{-12}	2.0	F11
$OH + HCl \rightarrow H_2O + Cl$	2.6×10^{-12}	350±100	8.0×10^{-13}	1.2	F12
$OH + HOCl \rightarrow H_2O + ClO$	3.0×10^{-12}	500±500	5.0×10^{-13}	3.0	F13
$OH + ClNO_2 \rightarrow HOCl + NO_2$	2.4×10^{-12}	1250±300	3.6×10^{-14}	2.0	F14
$OH + ClONO_2 \rightarrow$ products	1.2×10^{-12}	330±200	3.9×10^{-13}	1.5	F15
$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$	4.0×10^{-12}	1400±250	3.6×10^{-14}	1.2	F16
$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$	3.8×10^{-12}	1050±150	1.1×10^{-13}	1.4	F17
$OH + CHCl_3 \rightarrow CCl_3 + H_2O$	2.0×10^{-12}	900±150	1.0×10^{-13}	1.2	F18
$OH + CCl_4 \rightarrow$ products	$\sim 1.0 \times 10^{-12}$	>2300	$<5.0 \times 10^{-16}$	-	F19
$OH + CFCl_3 \rightarrow$ products (CFC-11)	$\sim 1.0 \times 10^{-12}$	>3700	$<5.0 \times 10^{-18}$	-	F20

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$OH + CF_2Cl_2 \rightarrow$ products (CFC-12)	$\sim 1.0 \times 10^{-12}$	>3600	$<6.0 \times 10^{-18}$	-	F21
$OH + CH_2ClF \rightarrow CHClF + H_2O$ (HCFC-31)	2.8×10^{-12}	1270±200	3.9×10^{-14}	1.2	F22
$OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$ (HCFC-21)	1.7×10^{-12}	1250±150	2.6×10^{-14}	1.2	F23
$OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$ (HCFC-22)	1.0×10^{-12}	1600±150	4.7×10^{-15}	1.1	F24
$OH + CH_3Cl \rightarrow$ products	2.4×10^{-12}	360±200	7.2×10^{-13}	3.0	F25
$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$ (HCC-140)	1.8×10^{-12}	1550±150	1.0×10^{-14}	1.1	F26
$OH + C_2HCl_3 \rightarrow$ products	4.9×10^{-13}	-(450±200)	2.2×10^{-12}	1.25	F27
$OH + C_2Cl_4 \rightarrow$ products	9.4×10^{-12}	1200±200	1.7×10^{-13}	1.25	F28
$OH + CCl_3CHO \rightarrow H_2O + CCl_3CO$	8.2×10^{-12}	600±300	1.1×10^{-12}	1.5	F29
$OH + CH_3CFCl_2 \rightarrow CH_2CFCl_2 + H_2O$ (HCFC-141b)	1.7×10^{-12}	1700±150	5.7×10^{-15}	1.2	F30
$OH + CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$ (HCFC-142b)	1.3×10^{-12}	1800±150	3.1×10^{-15}	1.2	F31
$OH + CH_2ClCF_2Cl \rightarrow CHClCF_2Cl + H_2O$ (HCFC-132b)	3.6×10^{-12}	1600±400	1.7×10^{-14}	2.0	F32
$OH + CHCl_2CF_2Cl \rightarrow CCl_2CF_2Cl + H_2O$ (HCFC-122)	1.0×10^{-12}	900±150	4.9×10^{-14}	1.2	F33
$OH + CHFClCFCl_2 \rightarrow CFClCFCl_2 + H_2O$ (HCFC-122a)	1.0×10^{-12}	1250±150	1.5×10^{-14}	1.1	F34
$OH + CH_2ClCF_3 \rightarrow CHClCF_3 + H_2O$ (HCFC-133a)	5.2×10^{-13}	1100±300	1.3×10^{-14}	1.3	F35
$OH + CHCl_2CF_3 \rightarrow CCl_2CF_3 + H_2O$ (HCFC-123)	7.0×10^{-13}	900±150	3.4×10^{-14}	1.2	F36
$OH + CHFClCF_2Cl \rightarrow CFClCF_2Cl + H_2O$ (HCFC-123a)	9.2×10^{-13}	1280±150	1.3×10^{-14}	1.2	F37
$OH + CHFClCF_3 \rightarrow CFClCF_3 + H_2O$ (HCFC-124)	8.0×10^{-13}	1350±150	8.6×10^{-15}	1.2	F38
$OH + CH_3CF_2CFCl_2 \rightarrow$ products (HCFC-243cc)	7.7×10^{-13}	1700±300	2.6×10^{-15}	2.0	F39

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$OH + CF_3CF_2CHCl_2 \rightarrow$ products (HCFC-225ca)	1.0×10^{-12}	1100±200	2.5×10^{-14}	1.3	F40
$OH + CF_2ClCF_2CHFCl \rightarrow$ products (HCFC-225cb)	5.5×10^{-13}	1250±200	8.3×10^{-15}	1.3	F41
$HO_2 + Cl \rightarrow HCl + O_2$	1.8×10^{-11}	-(170±200)	3.2×10^{-11}	1.5	F42
$\rightarrow OH + ClO$	4.1×10^{-11}	450±200	9.1×10^{-12}	2.0	F42
$HO_2 + ClO \rightarrow HOCl + O_2$	4.8×10^{-13}	$-(700\pm\frac{250}{700})$	5.0×10^{-12}	1.4	F43
$H_2O + ClONO_2 \rightarrow$ products	-	-	$<2.0\times10^{-21}$	-	F44
$NO + OClO \rightarrow NO_2 + ClO$	2.5×10^{-12}	600±300	3.4×10^{-13}	2.0	F45
$NO + Cl_2O_2 \rightarrow$ products	-	-	$<2.0\times10^{-14}$	-	F46
$NO_3 + OClO \xrightarrow{M} O_2ClONO_2$	(See Table 2)				
$NO_3 + HCl \rightarrow HNO_3 + Cl$	-	-	$<5.0\times10^{-17}$	-	F47
$HO_2NO_2 + HCl \rightarrow$ products	-	-	$<1.0\times10^{-21}$	-	F48
$Cl + O_2 \xrightarrow{M} ClOO$	(See Table 2)				
$Cl + O_3 \rightarrow ClO + O_2$	2.9×10^{-11}	260±100	1.2×10^{-11}	1.15	F49
$Cl + H_2 \rightarrow HCl + H$	3.7×10^{-11}	2300±200	1.6×10^{-14}	1.25	F50
$Cl + H_2O_2 \rightarrow HCl + HO_2$	1.1×10^{-11}	980±500	4.1×10^{-13}	1.5	F51
$Cl + NO \xrightarrow{M} NOCl$	(See Table 2)				
$Cl + NO_2 \xrightarrow{M} ClONO\ (ClNO_2)$	(See Table 2)				
$Cl + NO_3 \rightarrow ClO + NO_2$	2.4×10^{-11}	0±400	2.4×10^{-11}	1.5	F52
$Cl + N_2O \rightarrow ClO + N_2$	(See Note)				F53
$Cl + HNO_3 \rightarrow$ products	-	-	$<2.0\times10^{-16}$	-	F54
$Cl + CO \xrightarrow{M} ClCO$	(See Table 2)				
$Cl + CH_4 \rightarrow HCl + CH_3$	1.1×10^{-11}	1400±150	1.0×10^{-13}	1.1	F55
$Cl + CH_3D \rightarrow$ products				2.0	F56
$Cl + H_2CO \rightarrow HCl + HCO$	8.1×10^{-11}	30±100	7.3×10^{-11}	1.15	F57

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$Cl + CH_3O_2 \rightarrow$ products	-	-	$1.6x10^{-10}$	1.5	F58
$Cl + CH_3OH \rightarrow CH_2OH + HCl$	$5.4x10^{-11}$	0±250	$5.4x10^{-11}$	1.5	F59
$Cl + C_2H_2 \xrightarrow{M} ClC_2H_2$	(See Table 2)				
$Cl + C_2H_4 \xrightarrow{M} ClC_2H_4$	(See Table 2)				
$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	$7.7x10^{-11}$	90±90	$5.7x10^{-11}$	1.1	F60
$Cl + C_2H_5O_2 \rightarrow ClO + C_2H_5O$	-	-	$7.4x10^{-11}$	2.0	F61
$\rightarrow HCl + C_2H_4O_2$	-	-	$7.7x10^{-11}$	2.0	F61
$Cl + CH_3CN \rightarrow$ products	$1.6x10^{-11}$	2140±500	$1.2x10^{-14}$	2.0	F62
$Cl + CH_3CO_3NO_2 \rightarrow$ products	-	-	$<1x10^{-14}$		F63
$Cl + C_3H_8 \rightarrow HCl + C_3H_7$	$1.2x10^{-10}$	-(40±250)	$1.4x10^{-10}$	1.3	F64
$Cl + OClO \rightarrow ClO + ClO$	$3.4x10^{-11}$	-(160±200)	$5.8x10^{-11}$	1.25	F65
$Cl + ClOO \rightarrow Cl_2 + O_2$	$2.3x10^{-10}$	0±250	$2.3x10^{-10}$	3.0	F66
$\rightarrow ClO + ClO$	$1.2x10^{-11}$	0±250	$1.2x10^{-11}$	3.0	F66
$Cl + Cl_2O \rightarrow Cl_2 + ClO$	$6.2x10^{-11}$	-(130±130)	$9.6x10^{-11}$	1.2	F67
$Cl + Cl_2O_2 \rightarrow$ products	-	-	$1.0x10^{-10}$	2.0	F68
$Cl + HOCl \rightarrow$ products	$2.5x10^{-12}$	130±250	$1.6x10^{-12}$	1.5	F69
$Cl + ClNO \rightarrow NO + Cl_2$	$5.8x10^{-11}$	-(100±200)	$8.1x10^{-11}$	1.5	F70
$Cl + ClONO_2 \rightarrow$ products	$6.5x10^{-12}$	-(135±50)	$1.0x10^{-11}$	1.2	F71
$Cl + CH_3Cl \rightarrow CH_2Cl + HCl$	$3.2x10^{-11}$	1250±200	$4.8x10^{-13}$	1.2	F72
$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$	$3.1x10^{-11}$	1350±500	$3.3x10^{-13}$	1.5	F73
$Cl + CHCl_3 \rightarrow HCl + CCl_3$	$8.2x10^{-12}$	1325±500	$9.6x10^{-14}$	1.3	F74
$Cl + CH_3F \rightarrow HCl + CH_2F$ (HFC-41)	$2.0x10^{-11}$	1200±500	$3.5x10^{-13}$	1.3	F75
$Cl + CH_2F_2 \rightarrow HCl + CHF_2$ (HFC-32)	$1.2x10^{-11}$	1690±500	$5.0x10^{-14}$	1.5	F76
$Cl + CF_3H \rightarrow HCl + CF_3$ (HFC-23)	-	-	$3.0x10^{-18}$	5.0	F77

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$Cl + CH_2FCl \rightarrow HCl + CHFCl$ (HCFC-31)	$1.2x10^{-11}$	1390±500	$1.1x10^{-13}$	2.0	F78
$Cl + CHFCl_2 \rightarrow HCl + CFCl_2$ (HCFC-21)					
$Cl + CHF_2Cl \rightarrow HCl + CF_2Cl$ (HCFC-22)					
$Cl + CH_3CCl_3 \rightarrow CH_2CCl_3 + HCl$					
$Cl + CH_3CH_2F \rightarrow HCl + CH_3CHF$ (HFC-161)	$1.8x10^{-11}$	290±500	$6.8x10^{-12}$	3.0	F82
$\rightarrow HCl + CH_2CH_2F$	$1.4x10^{-11}$	880±500	$7.3x10^{-13}$	3.0	F82
$Cl + CH_3CHF_2 \rightarrow HCl + CH_3CF_2$ (HFC-152a)	$6.4x10^{-12}$	950±500	$2.6x10^{-13}$	1.3	F83
$\rightarrow HCl + CH_2CHF_2$	$7.2x10^{-12}$	2390±500	$2.4x10^{-15}$	3.0	F83
$Cl + CH_2FCH_2F \rightarrow HCl + CHFCH_2F$ (HFC-152)	$2.6x10^{-11}$	1060±500	$7.5x10^{-13}$	3.0	F84
$Cl + CH_3CFCl_2 \rightarrow HCl + CH_2CFCl_2$ (HCFC-141b)				1.2	
$Cl + CH_3CF_2Cl \rightarrow HCl + CH_2CF_2Cl$ (HCFC-142b)					
$Cl + CH_3CF_3 \rightarrow HCl + CH_2CF_3$ (HFC-143a)	$1.2x10^{-11}$	3880±500	$2.6x10^{-17}$	5.0	F87
$Cl + CH_2FCHF_2 \rightarrow HCl + CH_2FCF_2$ (HFC-143)	$5.5x10^{-12}$	1610±500	$2.5x10^{-14}$	3.0	F88
$\rightarrow HCl + CHFCHF_2$	$7.7x10^{-12}$	1720±500	$2.4x10^{-14}$	3.0	F88
$Cl + CH_2ClCF_3 \rightarrow HCl + CHClCF_3$ (HCFC-133a)	$1.8x10^{-12}$	1710±500	$5.9x10^{-15}$	3.0	F89
$Cl + CH_2FCF_3 \rightarrow HCl + CHFCF_3$ (HFC-134a)	-	-	$1.5x10^{-15}$	1.2	F90
$Cl + CHF_2CHF_2 \rightarrow HCl + CF_2CHF_2$ (HCF-134)	$7.5x10^{-12}$	2430±500	$2.2x10^{-15}$	1.5	F91
$Cl + CHCl_2CF_3 \rightarrow HCl + CCl_2CF_3$ (HCFC-123)	$4.4x10^{-12}$	1750±500	$1.2x10^{-14}$	1.3	F92
$Cl + CHFClCF_3 \rightarrow HCl + CFClCF_3$ (HCFC-124)	$1.1x10^{-12}$	1800±500	$2.7x10^{-15}$	1.3	F93
$Cl + CHF_2CF_3 \rightarrow HCl + CF_2CF_3$ (HFC-125)	-	-	$2.4x10^{-16}$	1.3	F94

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$ClO + O_3 \rightarrow ClOO + O_2$	-	-	$<1.4\times10^{-17}$	-	F95
$\rightarrow OClO + O_2$	1.0×10^{-12}	>4000	$<1.0\times10^{-18}$	-	F95
$ClO + H_2 \rightarrow$ products	$\sim1.0\times10^{-12}$	>4800	$<1.0\times10^{-19}$	-	F96
$ClO + NO \rightarrow NO_2 + Cl$	6.4×10^{-12}	-(290±100)	1.7×10^{-11}	1.15	F97
$ClO + NO_2 \xrightarrow{M} ClONO_2$	(See Table 2)				
$ClO + NO_3 \rightarrow ClOO + NO_2$	4.7×10^{-13}	0±400	4.7×10^{-13}	1.5	F98
$ClO + N_2O \rightarrow$ products	$\sim1.0\times10^{-12}$	>4300	$<6.0\times10^{-19}$	-	F99
$ClO + CO \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<4.0\times10^{-18}$	-	F100
$ClO + CH_4 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<4.0\times10^{-18}$	-	F101
$ClO + H_2CO \rightarrow$ products	$\sim1.0\times10^{-12}$	>2100	$<1.0\times10^{-15}$	-	F102
$ClO + CH_3O_2 \rightarrow$ products	3.3×10^{-12}	115±115	2.2×10^{-12}	1.5	F103
$ClO + ClO \rightarrow Cl_2 + O_2$	1.0×10^{-12}	1590±300	4.8×10^{-15}	1.5	F104
$\rightarrow ClOO + Cl$	3.0×10^{-11}	2450±500	8.0×10^{-15}	1.5	F104
$\rightarrow OClO + Cl$	3.5×10^{-13}	1370±300	3.5×10^{-15}	1.5	F104
$ClO + ClO \xrightarrow{M} Cl_2O_2$	(See Table 2)				
$ClO + OClO \xrightarrow{M} Cl_2O_3$	(See Table 2)				
$HCl + ClONO_2 \rightarrow$ products	-	-	$<1.0\times10^{-20}$	-	F105
$CH_2Cl + O_2 \xrightarrow{M} CH_2ClO_2$	(See Table 2)				
$CHCl_2 + O_2 \xrightarrow{M} CHCl_2O_2$	(See Table 2)				
$CCl_3 + O_2 \xrightarrow{M} CCl_3O_2$	(See Table 2)				
$CFCl_2 + O_2 \xrightarrow{M} CFCl_2O_2$	(See Table 2)				
$CF_2Cl + O_2 \xrightarrow{M} CF_2ClO_2$	(See Table 2)				
$CCl_3O_2 + NO_2 \xrightarrow{M} CCl_3O_2NO_2$	(See Table 2)				
$CFCl_2O_2 + NO_2 \xrightarrow{M} CFCl_2O_2NO_2$	(See Table 2)				

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$CF_2ClO_2 + NO_2 \xrightarrow{M} CF_2ClO_2NO_2$	(See Table 2)				
$CH_2ClO + O_2 \rightarrow CHClO + HO_2$	-	-	6×10^{-14}	5	F106
$CH_2ClO_2 + HO_2 \rightarrow CH_2ClO_2H + O_2$	3.3×10^{-13}	-(820±200)	5.2×10^{-12}	1.5	F107
$CH_2ClO_2 + NO \rightarrow CH_2ClO + NO_2$	7×10^{-12}	-(300±200)	1.9×10^{-11}	1.5	F108
$CCl_3O_2 + NO \rightarrow CCl_2O + NO_2 + Cl$	7.3×10^{-12}	-(270±200)	1.8×10^{-11}	1.3	F109
$CCl_2FO_2 + NO \rightarrow CClFO + NO_2 + Cl$	4.5×10^{-12}	-(350±200)	1.5×10^{-11}	1.3	F110
$CClF_2O_2 + NO \rightarrow CF_2O + NO_2 + Cl$	3.8×10^{-12}	-(400±200)	1.5×10^{-11}	1.2	F111
<u>BrO_X Reactions</u>					
$O + BrO \rightarrow Br + O_2$	[illegible]			1.5	[illegible]
$O + HBr \rightarrow OH + Br$	5.8×10^{-12}	1500±200	3.8×10^{-14}	1.3	G 2
$O + HOBr \rightarrow OH + BrO$	[illegible]				
$OH + Br_2 \rightarrow HOBr + Br$	4.2×10^{-11}	0±600	4.2×10^{-11}	1.3	G 4
$OH + BrO \rightarrow$ products	-	-	[illegible]		
$OH + HBr \rightarrow H_2O + Br$	1.1×10^{-11}	0±250	1.1×10^{-11}	1.2	[illegible]
$OH + CH_3Br \rightarrow CH_2Br + H_2O$	4.0×10^{-12}	1470±150	2.9×10^{-14}	1.1	G 7
$OH + CH_2Br_2 \rightarrow CHBr_2 + H_2O$	[illegible]				
[illegible]					
$OH + CHF_2Br \rightarrow CF_2Br + H_2O$	1.1×10^{-12}	1400±200	1.0×10^{-14}	1.1	G10
[illegible]					
$OH + CF_2ClBr \rightarrow$ products	-	-	$<1.5 \times 10^{-16}$	-	G12
$OH + CF_2Br_2 \rightarrow$ products	-	-	$<5.0 \times 10^{-16}$	-	G13
$OH + CF_3Br \rightarrow$ products	-	-	$<1.2 \times 10^{-16}$	-	G14
[illegible]					
[illegible]					
[illegible]					

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$OH + CF_2BrCHFCl \rightarrow CF_2BrCFCl + H_2O$	9.3×10^{-13}	1250±150	1.4×10^{-14}	1.5	G18
$OH + CF_2BrCF_2Br \rightarrow$ products	-	-	$<1.5 \times 10^{-16}$	-	G19
$HO_2 + Br \rightarrow HBr + O_2$	1.5×10^{-11}	600±600	2.0×10^{-12}	2.0	G20
$HO_2 + BrO \rightarrow$ products	3.4×10^{-12}	-(540±200)	2.1×10^{-11}	1.5	G21
$NO_3 + HBr \rightarrow HNO_3 + Br$	-	-	$<1.0 \times 10^{-16}$	-	G22
$Cl + CH_2ClBr \rightarrow HCl + CHClBr$	4.3×10^{-11}	1370±500	4.3×10^{-13}	3.0	G23
$Cl + CH_3Br \rightarrow HCl + CH_2Br$	1.5×10^{-11}	1060±100	4.3×10^{-13}	1.2	G24
$Cl + CH_2Br_2 \rightarrow HCl + CHBr_2$	6.4×10^{-12}	810±100	4.2×10^{-13}	1.2	G25
$Br + O_3 \rightarrow BrO + O_2$	1.7×10^{-11}	800±200	1.2×10^{-12}	1.2	G26
$Br + H_2O_2 \rightarrow HBr + HO_2$	1.0×10^{-11}	>3000	$<5.0 \times 10^{-16}$	-	G27
$Br + NO_2 \xrightarrow{M} BrNO_2$	(See Table 2)				
$Br + NO_3 \rightarrow BrO + NO_2$	-	-	1.6×10^{-11}	2.0	G28
$Br + H_2CO \rightarrow HBr + HCO$	1.7×10^{-11}	800±200	1.1×10^{-12}	1.3	G29
$Br + OClO \rightarrow BrO + ClO$	2.6×10^{-11}	1300±300	3.4×10^{-13}	2.0	G30
$Br + Cl_2O \rightarrow BrCl + ClO$	2.1×10^{-11}	470±150	4.3×10^{-12}	1.3	G31
$Br + Cl_2O_2 \rightarrow$ products	-	-	3.0×10^{-12}	2.0	G32
$BrO + O_3 \rightarrow$ products	$\sim 1.0 \times 10^{-12}$	>3200	$<2.0 \times 10^{-17}$	-	G33
$BrO + NO \rightarrow NO_2 + Br$	8.8×10^{-12}	-(260±130)	2.1×10^{-11}	1.15	G34
$BrO + NO_2 \xrightarrow{M} BrONO_2$	(See Table 2)				
$BrO + NO_3 \rightarrow$ products	-	-	1.0×10^{-12}	3.0	G35
$BrO + ClO \rightarrow Br + OClO$	1.6×10^{-12}	-(430±200)	6.8×10^{-12}	1.25	G36
$\rightarrow Br + ClOO$	2.9×10^{-12}	-(220±200)	6.1×10^{-12}	1.25	G36
$\rightarrow BrCl + O_2$	5.8×10^{-13}	-(170±200)	1.0×10^{-12}	1.25	G36
$BrO + BrO \rightarrow$ products	1.5×10^{-12}	-(230±150)	3.2×10^{-12}	1.15	G37
$CH_2BrO + O_2 \rightarrow CHBrO + HO_2$			6×10^{-14}	10	G38

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$CH_2BrO_2 + NO \rightarrow CH_2BrO + NO_2$	$4x10^{-12}$	-(300±200)	1.1×10^{-11}	1.5	G39
<u>IO_x Reactions</u>					
$O + I_2 \rightarrow IO + I$	$1.4x10^{-10}$	0±250	$1.4x10^{-10}$		
$O + IO \rightarrow O_2 + I$					
$OH + I_2 \rightarrow HOI + I$			$1.8x10^{-10}$	2.0	H 3
$OH + HI \rightarrow H_2O + I$			$3.0x10^{-11}$	2.0	H 4
$OH + CH_3I \rightarrow H_2O + CH_2I$	$3.1x10^{-12}$	1120±500	$7.2x10^{-14}$	3.0	H 5
$OH + CF_3I \rightarrow HOI + CF_3$			$3.1x10^{-14}$	5.0	H 6
$HO_2 + I \rightarrow HI + O_2$	$1.5x10^{-11}$	1090±500	$3.8x10^{-13}$	2.0	H 7
$HO_2 + IO \rightarrow HOI + O_2$			$8.4x10^{-11}$	1.5	H 8
$NO_3 + HI \rightarrow HNO_3 + I$	(See Note)				H 9
$I + O_3 \rightarrow IO + O_2$					
$I + NO \xrightarrow{M} INO$	(See Table 2)				
$I + NO_2 \xrightarrow{M} INO_2$	(See Table 2)				
$IO + NO \rightarrow I + NO_2$					
$IO + NO_2 \xrightarrow{M} IONO_2$	(See Table 2)				
$IO + IO \rightarrow$ products					
$INO + INO \rightarrow I_2 + 2NO$	$8.4x10^{-11}$	2620±600	$1.3x10^{-14}$	2.5	H16
$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	$2.9x10^{-11}$	2600±1000	$4.7x10^{-15}$	3.0	H17
<u>SO_x Reactions</u>					
$O + SH \rightarrow SO + H$	-	-	$1.6x10^{-10}$	5.0	I1
$O + CS \rightarrow CO + S$	$2.7x10^{-10}$	760±250	$2.1x10^{-11}$	1.1	I2
$O + H_2S \rightarrow OH + SH$	$9.2x10^{-12}$	1800±550	$2.2x10^{-14}$	1.7	I3

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$O + OCS \rightarrow CO + SO$	2.1×10^{-11}	2200±150	1.3×10^{-14}	1.2	[redacted]
$O + CS_2 \rightarrow CS + SO$	3.2×10^{-11}	650±150	3.6×10^{-12}	1.2	I5
$O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$	1.3×10^{-11}	-(410±100)	5.0×10^{-11}	1.1	[redacted]
$O + CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$	5.5×10^{-11}	-(250±100)	1.3×10^{-10}	1.3	
$O_3 + H_2S \rightarrow$ products	-	-	$<2.0\times10^{-20}$	-	I8
$O_3 + CH_3SCH_3 \rightarrow$ products	-	-	$<1.0\times10^{-18}$	-	I9
$O_3 + SO_2 \rightarrow SO_3 + O_2$	3.0×10^{-12}	>7000	$<2.0\times10^{-22}$	-	I10
$OH + H_2S \rightarrow SH + H_2O$	6.0×10^{-12}	75±75	4.7×10^{-12}	1.2	I11
$OH + OCS \rightarrow$ products	1.1×10^{-13}	1200±500	1.9×10^{-15}	2.0	I12
$OH + CS_2 \rightarrow$ products	(See Note)	-	-	-	[redacted]
[redacted]	9.9×10^{-12}	-(360±100)	3.3×10^{-11}	1.2	I14
$OH + CH_3SCH_3 \rightarrow H_2O + CH_2SCH_3$	1.2×10^{-11}	260±100	5.0×10^{-12}	1.15	[redacted]
$OH + CH_3SSCH_3 \rightarrow$ products	6.0×10^{-11}	-(400±200)	2.3×10^{-10}	1.2	
$OH + S \rightarrow H + SO$	-	-	6.6×10^{-11}	3.0	I17
$OH + SO \rightarrow H + SO_2$	-	-	8.6×10^{-11}	2.0	I18
$OH + SO_2 \xrightarrow{M} HOSO_2$	(See Table 2)				
$HO_2 + H_2S \rightarrow$ products	-	-	$<3.0\times10^{-15}$	-	I19
$HO_2 + CH_3SH \rightarrow$ products	-	-	$<4.0\times10^{-15}$	-	I19
$HO_2 + CH_3SCH_3 \rightarrow$ products	-	-	$<5.0\times10^{-15}$	-	I19
$HO_2 + SO_2 \rightarrow$ products	-	-	$<1.0\times10^{-18}$	-	I20
$NO_2 + SO_2 \rightarrow$ products	-	-	$<2.0\times10^{-26}$	-	I21
$NO_3 + H_2S \rightarrow$ products	-	-	$<8.0\times10^{-16}$	-	I22
$NO_3 + OCS \rightarrow$ products	-	-	$<1.0\times10^{-16}$	-	I23
$NO_3 + CS_2 \rightarrow$ products	-	-	$<4.0\times10^{-16}$	-	I24
$NO_3 + CH_3SH \rightarrow$ products	4.4×10^{-13}	-(210±210)	8.9×10^{-13}	1.25	I25
$NO_3 + CH_3SCH_3 \rightarrow CH_3SCH_2 + HNO_3$	1.9×10^{-13}	-(500±200)	1.0×10^{-12}	1.2	[redacted]

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$NO_3 + CH_3SSCH_3 \rightarrow$ products	$1.3x10^{-12}$	270±270	$5.3x10^{-13}$	1.4	I27
$NO_3 + SO_2 \rightarrow$ products	-	-	$<7.0x10^{-21}$	-	I28
$N_2O_5 + CH_3SCH_3 \rightarrow$ products	-	-	$<1.0x10^{-17}$	-	I29
$CH_3O_2 + SO_2 \rightarrow$ products	-	-	$<5.0x10^{-17}$	-	I30
[redacted]					
$Cl + H_2S \rightarrow HCl + SH$					
$Cl + OCS \rightarrow SCl + CO$	-	-	$<1.0x10^{-16}$	-	I33
$Cl + CS_2 \rightarrow$ products	-	-	$<4.0x10^{-15}$	-	I34
$Cl + CH_3SH \rightarrow CH_3S + HCl$	[redacted]				
$Cl + CH_3SCH_3 \rightarrow$ products	(See Note)	-	-	-	
$ClO + OCS \rightarrow$ products	-	-	$<2.0x10^{-16}$	-	I37
$ClO + CH_3SCH_3 \rightarrow$ products	-	-	$9.5x10^{-15}$	2.0	I38
$ClO + SO \rightarrow Cl + SO_2$	$2.8x10^{-11}$	0±50	$2.8x10^{-11}$	1.3	I39
$ClO + SO_2 \rightarrow Cl + SO_3$	-	-	$<4.0x10^{-18}$	-	I37
$Br + H_2S \rightarrow HBr + SH$	$1.4x10^{-11}$	2750±300	$1.4x10^{-15}$	2.0	I40
$Br + CH_3SH \rightarrow CH_3S + HBr$	$9.2x10^{-12}$	390±100	$2.5x10^{-12}$	2.0	I40
[redacted]					
$BrO + CH_3SCH_3 \rightarrow$ products					
$BrO + SO \rightarrow Br + SO_2$			$5.7x10^{-11}$	1.4	I43
$IO + CH_3SH \rightarrow$ products			$6.6x10^{-16}$	2.0	I44
$IO + CH_3SCH_3 \rightarrow$ products			$1.2x10^{-14}$	1.5	I45
$S + O_2 \rightarrow SO + O$	$2.3x10^{-12}$	0±200	$2.3x10^{-12}$	1.2	I46
$S + O_3 \rightarrow SO + O_2$			$1.2x10^{-11}$	2.0	I47
$SO + O_2 \rightarrow SO_2 + O$	$2.6x10^{-13}$	2400±500	$8.4x10^{-17}$	2.0	I48
$SO + O_3 \rightarrow SO_2 + O_2$	$3.6x10^{-12}$	1100±200	$9.0x10^{-14}$	1.2	I49
$SO + NO_2 \rightarrow SO_2 + NO$	$1.4x10^{-11}$	0±50	$1.4x10^{-11}$	1.2	I50

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$SO + OClO \rightarrow SO_2 + ClO$			1.9×10^{-12}	3.0	I51
$SO_3 + H_2O \rightarrow$ products	(See Note)		-	-	I52
$SO_3 + NH_3 \rightarrow$ products	(See Table 2)		-	-	I51
$SO_3 + NO_2 \rightarrow$ products			1.0×10^{-19}	10.0	I53
$SH + O_2 \rightarrow OH + SO$			$<4.0 \times 10^{-19}$	-	I54
$SH + O_3 \rightarrow HSO + O_2$	9.0×10^{-12}	280±200	3.5×10^{-12}	1.3	I55
$SH + H_2O_2 \rightarrow$ products			$<5.0 \times 10^{-15}$	-	I56
$SH + NO \xrightarrow{M} HSNO$	(See Table 2)				
$SH + NO_2 \rightarrow HSO + NO$	2.9×10^{-11}	(240±50)	6.5×10^{-11}	1.2	I57
$SH + Cl_2 \rightarrow ClSH + Cl$	1.7×10^{-11}	690±200	1.7×10^{-12}	2.0	I58
$SH + BrCl \rightarrow$ products	2.3×10^{-11}	-(350±200)	7.4×10^{-11}	2.0	I58
$SH + Br_2 \rightarrow BrSH + Br$	6.0×10^{-11}	-(160±160)	1.0×10^{-10}	2.0	I58
$SH + F_2 \rightarrow FSH + F$	4.3×10^{-11}	1390±200	4.0×10^{-13}	2.0	I58
$HSO + O_2 \rightarrow$ products			$<2.0 \times 10^{-17}$	-	I59
$HSO + O_3 \rightarrow$ products			1.0×10^{-13}	1.3	I60
$HSO + NO \rightarrow$ products			$<1.0 \times 10^{-15}$	-	I61
$HSO + NO_2 \rightarrow HSO_2 + NO$			9.6×10^{-12}	2.0	I61
$HSO_2 + O_2 \rightarrow HO_2 + SO_2$			3.0×10^{-13}	3.0	I62
$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	1.3×10^{-12}	330±200	4.4×10^{-13}	1.2	I63
$CS + O_2 \rightarrow OCS + O$			2.9×10^{-19}	2.0	I64
$CS + O_3 \rightarrow OCS + O_2$			3.0×10^{-16}	3.0	I65
$CS + NO_2 \rightarrow OCS + NO$			7.6×10^{-17}	3.0	I65
$CH_3S + O_2 \rightarrow$ products			$<3.0 \times 10^{-18}$	-	I66
$CH_3S + O_3 \rightarrow$ products	2.0×10^{-12}	-(290±100)	5.3×10^{-12}	1.15	I67
$CH_3S + NO \rightarrow$ products			$<1.0 \times 10^{-13}$	-	I68
$CH_3S + NO \xrightarrow{M}$ products	(See Table 2)				

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$CH_3S + NO_2 \rightarrow CH_3SO + NO$	$2.1x10^{-11}$	-(320±100)	$6.1x10^{-11}$	1.15	I69
$CH_2SH + O_2 \rightarrow$ products			$6.5x10^{-12}$	2.0	I70
$CH_2SH + O_3 \rightarrow$ products			$3.5x10^{-11}$	2.0	I71
$CH_2SH + NO \rightarrow$ products			$1.9x10^{-11}$	2.0	I72
$CH_2SH + NO_2 \rightarrow$ products			$5.2x10^{-11}$	2.0	I73
$CH_3SO + O_3 \rightarrow$ products			$6.0x10^{-13}$	1.5	I74
$CH_3SO + NO_2 \rightarrow CH_3SO_2 + NO$			$1.2x10^{-11}$	1.4	I75
$CH_3SOO + O_3 \rightarrow$ products			$<8.0x10^{-13}$	-	I76
$CH_3SOO + NO \rightarrow$ products	$1.1x10^{-11}$	0±100	$1.1x10^{-11}$	2.0	I76
[redacted]					
$CH_3SCH_2 + O_2 \xrightarrow{M} CH_3SCH_2O_2$	(See Table 2)				
$CH_3SCH_2 + NO_3 \rightarrow$ products			3.0×10^{-10}	2.0	I78
$CH_3SCH_2O_2 + NO \rightarrow CH_3SCH_2O + NO_2$			1.9×10^{-11}	2.0	I79
$CH_3SS + O_3 \rightarrow$ products			$4.6x10^{-13}$	2.0	I80
$CH_3SS + NO_2 \rightarrow$ products			$1.8x10^{-11}$	2.0	I81
$CH_3SSO + NO_2 \rightarrow$ products			$4.5x10^{-12}$	2.0	I81
Metal Reactions					
$Na + O_2 \xrightarrow{M} NaO_2$	(See Table 2)				
$Na + O_3 \rightarrow NaO + O_2$	[redacted]		$7.3x10^{-10}$	1.2	[redacted]
$\rightarrow NaO_2 + O$	-	-	$<4.0x10^{-11}$	-	
$Na + N_2O \rightarrow NaO + N_2$	$2.8x10^{-10}$	1600±400	$1.3x10^{-12}$	1.2	
$Na + Cl_2 \rightarrow NaCl + Cl$	$7.3x10^{-10}$	0±200	$7.3x10^{-10}$	1.3	J 3
$NaO + O \rightarrow Na + O_2$	$3.7x10^{-10}$	0±400	$3.7x10^{-10}$	3.0	J 4
$NaO + O_2 \xrightarrow{M} NaO_3$	(See Table 2)				
$NaO + O_3 \rightarrow NaO_2 + O_2$	[redacted]		$1.6x10^{-10}$	[redacted]	

TABLE 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)[a]	f(298)[b]	Notes[c]
$\rightarrow Na + 2O_2$	6.0×10^{-11}	0±800	6.0×10^{-11}	3.0	J 5
$NaO + H_2 \rightarrow NaOH + H$	2.6×10^{-11}	0±600	2.6×10^{-11}	2.0	J 6
$NaO + H_2O \rightarrow NaOH + OH$	2.2×10^{-10}	0±400	2.2×10^{-10}	2.0	J 7
$NaO + NO \rightarrow Na + NO_2$	1.5×10^{-10}	0±400	1.5×10^{-10}	4.0	J 8
$NaO + CO_2 \xrightarrow{M} NaCO_3$	(See Table 2)				
$NaO + HCl \rightarrow$ products	2.8×10^{-10}	0±400	2.8×10^{-10}	3.0	J 9
$NaO_2 + O \rightarrow NaO + O_2$	2.2×10^{-11}	0±600	2.2×10^{-11}	5.0	J10
$NaO_2 + NO \rightarrow NaO + NO_2$	-	-	$<10^{-14}$	-	J11
$NaO_2 + HCl \rightarrow$ products	2.3×10^{-10}	0±400	2.3×10^{-10}	3.0	J12
$NaOH + HCl \rightarrow NaCl + H_2O$	2.8×10^{-10}	0±400	2.8×10^{-10}	3.0	J13
$NaOH + CO_2 \xrightarrow{M} NaHCO_3$	(See Table 2)				

Shaded areas indicate changes or additions since JPL 92-20.

a Units are cm^3/molecule-sec.

b f(298) is the uncertainty factor at 298 K. To calculate the uncertainty at other temperatures, use the expression:

$$f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$$

Note that the exponent is absolute value.

c Notes refer to detailed information which are provided in the full NASA Data Panel report issued as a Jet Propulsion Laboratory publication.

TABLE 2. Rate Constants For Association Reactions

Reaction	Low Pressure Limit[a] $k_0(T) = k_0^{300}(T/300)^{-n}$ k_0^{300}	n	High Pressure Limit[b] $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$ k_∞^{300}	m	Notes[c]
		O_x Reactions			
$O + O_2 \xrightarrow{M} O_3$	(6.0±0.5) (-34)	2.3±0.5	-	-	A1
		$O(^1D)$ Reactions			
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(3.5±3.0) (-37)	$0.6\pm^{2.0}_{0.6}$	-	-	A2
		HO_x Reactions			
$H + O_2 \xrightarrow{M} HO_2$	(5.7±0.5) (-32)	1.6±0.5	(7.5±4.0) (-11)	0±1.0	B1
$OH + OH \xrightarrow{M} H_2O_2$	(6.2±1.2) (-31)	$1.0\pm^{2.0}_{1.0}$	(2.6±1.0) (-11)	0±0.5	B2
		NO_x Reactions			
$O + NO \xrightarrow{M} NO_2$	(9.0±2.0) (-32)	1.5±0.3	(3.0±1.0) (-11)	0±1.0	C1
$O + NO_2 \xrightarrow{M} NO_3$	(9.0±1.0) (-32)	2.0±1.0	(2.2±0.3) (-11)	0±1.0	C2
$OH + NO \xrightarrow{M} HONO$	(7.0±1.0) (-31)	2.6±0.3	(9.8±4.0) (-11)	0.4±0.5	C3
$OH + NO_2 \xrightarrow{M} HNO_3$ (See note)	(2.5±0.1) (-30)	4.4±0.3	(1.6±0.2) (-11)	1.7±0.2	C4
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(1.8±0.3) (-31)	3.2±0.4	(4.7±1.0) (-12)	1.4±1.4	C5
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(2.2±0.5) (-30)	3.9±1.0	(1.5±0.8) (-12)	0.7±0.4	C6
$NO_3 \xrightarrow{M} NO + O_2$	See Note				C7
		Hydrocarbon Reactions			
$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(4.5±1.5) (-31)	3.0±1.0	(1.8±0.2) (-12)	1.7±1.7	D1
$C_2H_5 + O_2 \xrightarrow{M} C_2H_5O_2$	(1.5±1.0) (-28)	3.0±1.0	(8.0±1.0) (-12)	0±1.0	D2
$OH + C_2H_2 \xrightarrow{M} HOCHCH$	(5.5±2.0) (-30)	0.0±0.2	(8.3±1.0) (-13)	$-2\pm^{2}_{1}$	D3
$OH + C_2H_4 \xrightarrow{M} HOCH_2CH_2$	(1.0±0.6) (-28)	0.8±2.0	(8.8±0.9) (-12)	$0\pm^{0}_{2}$	D4
$CH_3O + NO \xrightarrow{M} CH_3ONO$	(1.4±0.5) (-29)	3.8±1.0	(3.6±1.6) (-11)	0.6±1.0	D5

TABLE 2. (Continued)

Reaction	Low Pressure Limit[a] $k_0(T) = k_0^{300}(T/300)^{-n}$ k_0^{300}	n	High Pressure Limit[b] $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$ k_∞^{300}	m	Notes[c]
$CH_3O + NO_2 \xrightarrow{M} CH_3ONO_2$	(1.1±0.4) (-28)	4.0±2.0	(1.6±0.5) (-11)	1.0±1.0	D6
$C_2H_5O + NO \xrightarrow{M} C_2H_5ONO$	(2.8±1.0) (-27)	4.0±2.0	(5.0±1.0) (-11)	1.0±1.0	D7
$C_2H_5O + NO_2 \xrightarrow{M} C_2H_5ONO_2$	(2.0±1.0) (-27)	4.0±2.0	(2.8±0.4) (-11)	1.0±1.0	D8
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(1.5±0.8) (-30)	4.0±2.0	(6.5±3.2) (-12)	2.0±2.0	D9
$CH_3C(O)O_2 + NO_2 \xrightarrow{M} CH_3C(O)O_2NO_2$	(9.7±3.8) (-29)	5.6±2.8	(9.3±0.4)(-12)	1.5±0.3	D10
	FO_x Reactions				
$F + O_2 \xrightarrow{M} FO_2$	(4.4±0.4) (-33)	1.2±0.5	-	-	E1
$F + NO \xrightarrow{M} FNO$	(1.8±0.3) (-31)	1.0±10	(2.8±1.4) (-10)	0.0±1.0	E2
$F + NO_2 \xrightarrow{M} FNO_2$	(6.3±3.0) (-32)	2.0±2.0	(2.6±1.3) (-10)	0.0±1.0	E3
$FO + NO_2 \xrightarrow{M} FONO_2$	(2.6±2.0) (-31)	1.3±1.3	(2.0±1.0) (-11)	1.5±1.5	E4
$CF_3 + O_2 \xrightarrow{M} CF_3O_2$	(3.0±0.3) (-29)	4.0±2.0	(4.0±1.0) (-12)	1.0±1.0	E5
$CF_3O + NO_2 \xrightarrow{M} CF_3ONO_2$	See Note				E6
$CF_3O_2 + NO_2 \xrightarrow{M} CF_3O_2NO_2$	(2.2±0.5) (-29)	5.0±1.0	(6.0±1.0) (-12)	2.5±1.0	E7
$CF_3O + CO \xrightarrow{M} CF_3OCO$	(2.5±0.2) (-31)	-	(6.8±0.4) (-14)	-1.2	E8
$CF_3O \xrightarrow{M} CF_2O + F$	See Note				E9
	ClO_x Reactions				
$Cl + O_2 \xrightarrow{M} ClOO$	(2.7±1.0) (-33)	1.5±0.5	-	-	F1
$Cl + NO \xrightarrow{M} ClNO$	(9.0±2.0) (-32)	1.6±0.5	-	-	F2
$Cl + NO_2 \xrightarrow{M} ClONO$	(1.3±0.2) (-30)	2.0±1.0	(1.0±0.5) (-10)	1.0±1.0	F3
$\xrightarrow{M} ClNO_2$	(1.8±0.3) (-31)	2.0±1.0	(1.0±0.5) (-10)	1.0±1.0	

TABLE 2. (Continued)

Reaction	Low Pressure Limit[a] $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit[b] $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		Notes[c]
	k_o^{300}	n	k_∞^{300}	m	
$Cl + CO \xrightarrow{M} ClCO$	(1.3±0.5) (-33)	3.8±0.5	-	-	F4
$Cl + C_2H_2 \xrightarrow{M} ClC_2H_2$	[redacted]	2.1±1.0	(2.1±0.4) (-10)	1.0±0.5	[redacted]
$Cl + C_2H_4 \xrightarrow{M} ClC_2H_4$	(1.6±1) (-29)	[redacted]	(3.1±2) (-10)	1.0±0.5	[redacted]
[redacted]					
$ClO + NO_2 \xrightarrow{M} ClONO_2$	(1.8±0.3) (-31)	3.4±1.0	(1.5±0.7) (-11)	1.9±1.9	F8
$OClO + NO_3 \xrightarrow{M} O_2ClONO_2$	See Note				[redacted]
$ClO + ClO \xrightarrow{M} Cl_2O_2$	(2.2±0.4) (-32)	3.1±0.5	(3.5±2) (-12)	1.0±1.0	F10
$ClO + OClO \xrightarrow{M} Cl_2O_3$	(6.2±1.0) (-32)	4.7±0.6	(2.4±1.2) (-11)	0±1.0	[redacted]
$OClO + O \xrightarrow{M} ClO_3$	(1.9±0.5) (-31)	1.1±1.0	(3.1±0.8) (-11)	0±1.0	F12
$CH_2Cl + O_2 \xrightarrow{M} CH_2ClO_2$	(1.9±0.1) (-30)	3.2±0.2	(2.9±0.2) (-12)	1.2±0.6	F13
$CHCl_2 + O_2 \xrightarrow{M} CHCl_2O_2$	(1.3±0.1) (-30)	4.0±0.2	(2.8±0.2) (-12)	1.4±0.6	F14
$CCl_3 + O_2 \xrightarrow{M} CCl_3O_2$	(6.9±0.2) (-31)	6.4±0.3	(2.4±0.2) (-12)	2.1±0.6	F15
$CFCl_2 + O_2 \xrightarrow{M} CFCl_2O_2$	(5.0±0.8) (-30)	4.0±2.0	(6.0±1.0) (-12)	1.0±1.0	F16
$CF_2Cl + O_2 \xrightarrow{M} CF_2ClO_2$	(3.0±1.5) (-30)	4.0±2.0	(3±2) (-12)	1.0±1.0	F17
$CCl_3O_2 + NO_2 \xrightarrow{M} CCl_3O_2NO_2$	(5.0±1.0) (-29)	5.0±1.0	(6.0±1.0) (-12)	2.5±1.0	F18
$CFCl_2O_2 + NO_2 \xrightarrow{M} CFCl_2O_2NO_2$	(3.5±0.5) (-29)	5.0±1.0	(6.0±1.0) (-12)	2.5±1.0	F19
$CF_2ClO_2 + NO_2 \xrightarrow{M} CF_2ClO_2NO_2$	(3.3±0.7) (-29)	6.7±1.3	(4.1±1.9) (-12)	2.8±0.7	F20
	BrO_x Reactions				
$Br + NO_2 \xrightarrow{M} BrNO_2$	(4.2±0.8) (-31)	2.4±0.5	(2.7±0.5) (-11)	0±1.0	G1
$BrO + NO_2 \xrightarrow{M} BrONO_2$	(5.2±0.6) (-31)	3.2±0.8	(6.9±1.0) (-12)	2.9±1.0	G2

TABLE 2. (Continued)

Reaction	Low Pressure Limit[a] $k_0(T) = k_0^{300}(T/300)^{-n}$ k_0^{300}	n	High Pressure Limit[b] $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$ k_∞^{300}	m	Notes[c]
		IO_x Reactions			
$I + NO \xrightarrow{M} INO$	(1.8±0.5) (-32)	1.0±0.5	(1.7±1.0) (-11)	0±1.0	H1
$I + NO_2 \xrightarrow{M} INO_2$	(3.0±1.5) (-31)	1.0±1.0	(6.6±5.0) (-11)	0±1.0	H2
$IO + NO_2 \xrightarrow{M} IONO_2$	(5.9±2.0) (-31)	3.5±1.0	(9.0±1.0) (-12)	1.5±1.0	H3
		SO_x Reactions			
$HS + NO \xrightarrow{M} HSNO$	(2.4±0.4) (-31)	3.0±1.0	(2.7±0.5) (-11)	$0\pm^{0}_{2}$	I1
$CH_3S + NO \xrightarrow{M} CH_3SNO$	(3.2±0.4) (-29)	4.0±1.0	(3.9±0.6) (-11)	2.7±1.0	I2
$O + SO_2 \xrightarrow{M} SO_3$	$(1.3\pm^{1.3}_{0.7})$ (-33)	3.6±0.7			I3
$OH + SO_2 \xrightarrow{M} HOSO_2$	(3.0±1.0) (-31)	3.3±1.5	(1.5±0.5) (-12)	$0\pm^{0}_{2}$	I4
$CH_3SCH_2 + O_2 \xrightarrow{M} CH_3SCH_2O_2$	See Note				I5
$SO_3 + NH_3 \xrightarrow{M} H_3NSO_3$	(3.9±0.8) (-30)	3.0±3.0	(4.7±1.3) (-11)	0±1.0	I6
		Metal Reactions			
$Na + O_2 \xrightarrow{M} NaO_2$	(3.2±0.3) (-30)	1.4±0.3	(6.0±2.0) (-10)	0±1.0	J1
$NaO + O_2 \xrightarrow{M} NaO_3$	(3.5±0.7) (-30)	2.0±2.0	(5.7±3.0) (-10)	0±1.0	J2
$NaO + CO_2 \xrightarrow{M} NaCO_3$	(8.7±2.6) (-28)	2.0±2.0	(6.5±3.0) (-10)	0±1.0	J3
$NaOH + CO_2 \xrightarrow{M} NaHCO_3$	(1.3±0.3) (-28)	2.0±2.0	(6.8±4.0) (-10)	0±1.0	J4

Note: $k(Z) = k(M,T) = \left(\frac{k_0(T)[M]}{1 + (k_0(T)[M]/k_\infty(T))}\right) 0.6^{\{1 + [\log_{10}(k_0(T)[M]/k_\infty(T))]^2\}^{-1}}$

The values quoted are suitable for air as the third body, M.

a Units are $cm^6/molecule^2$-sec.

b Units are $cm^3/molecule$-sec.

c Notes refer to detailed information which are provided in the full NASA Data Panel Report issued as a Jet Propulsion Laboratory publication.

Shaded areas indicate changes or additions since JPL 94-26.

TABLE 3. Equilibrium Constants

Reaction	A/cm^3 molecule^{-1}	B±ΔB/°K	K_{eq}(298 K)	f(298 K)[a]	Note[b]
$HO_2 + NO_2 \rightarrow HO_2NO_2$	2.1×10^{-27}	10900±1000	1.6×10^{-11}	5	1
$NO + NO_2 \rightarrow N_2O_3$	3.3×10^{-27}	4667±100	2.1×10^{-20}	2	2
$NO_2 + NO_2 \rightarrow N_2O_4$	5.9×10^{-29}	6643±250	2.5×10^{-19}	2	3
$NO_2 + NO_3 \rightarrow N_2O_5$	2.7×10^{-27}	11000±500	2.9×10^{-11}	1.3	4
$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$	1.3×10^{-28}	11200±1000	2.7×10^{-12}	2	5
$CH_3C(O)O_2 + NO_2 \rightarrow CH_3C(O)O_2NO_2$	9.0×10^{-29}	14000±200	2.5×10^{-8}	2	6
$F + O_2 \rightarrow FOO$	3.2×10^{-25}	6100±1200	2.5×10^{-16}	10	7
$Cl + O_2 \rightarrow ClOO$	5.7×10^{-25}	2500±750	2.5×10^{-21}	2	8
$Cl + CO \rightarrow ClCO$	1.6×10^{-25}	4000±500	1.1×10^{-19}	5	9
$ClO + O_2 \rightarrow ClO{\cdot}O_2$	2.9×10^{-26}	<3700	$<7.2\times10^{-21}$	-	10
$ClO + ClO \rightarrow Cl_2O_2$	1.3×10^{-27}	8744±850	7.2×10^{-15}	1.5	11
$ClO + OClO \rightarrow Cl_2O_3$	1.1×10^{-24}	5455±300	9.8×10^{-17}	3	12
$OClO + NO_3 \rightarrow O_2ClONO_2$	1×10^{-28}	9300±1000	3.6×10^{-15}	5	13
$OH + CS_2 \rightarrow CS_2OH$	4.5×10^{-25}	5140±500	1.4×10^{-17}	1.4	14
$CH_3S + O_2 \rightarrow CH_3SO_2$	1.8×10^{-27}	5545±300	2.2×10^{-19}	1.4	15

K/cm^3 molecule^{-1} = A exp (B/T) [200 < T/K < 300]

[a] f(298) is the uncertainty factor at 298 K. To calculate the uncertainty at other temperatures, use the expression:

$$f(T) = f(298\ K)\ \exp\left[\ \Delta B\ \left(\frac{1}{T} - \frac{1}{298}\right)\ \right].$$

Shaded areas indicate changes or additions since JPL 94-26

[b] Notes refer to detailed information which are provided in the full NASA Data Panel Report issued as a Jet Propulsion Laboratory publication.

SECTION H

ATMOSPHERIC OZONE RESEARCH

EXECUTIVE SUMMARY

NASA maintains an extensive research program related to atmospheric ozone in order to provide high quality scientific data on both the troposphere and stratosphere to the scientific community and to policy-makers who use such information in setting environmental policy. NASA takes a distinctly global viewpoint in this research, making observations over all parts of the Earth and heavily utilizing global models. NASA research in this area has been a major contributor to the overall effort involving other US Government agencies, scientists from academia, industry, and government, as well as foreign entities. These efforts address the science agendas developed through peer-led groups, notably the International Global Atmospheric Chemistry (IGAC) Program of the International Geosphere-Biosphere Programme (IGBP) and the Stratospheric Processes and their Role in Climate (SPARC) group of the World Climate Research Programme (WCRP). NASA managers, researchers, and grantees have played significant roles in internationally-sponsored assessments such as the World Meteorological Organization/United Nations Environment Programme *Scientific Assessment of Ozone Depletion* and the *Climate Change* assessments of the Intergovernmental Panel on Climate Change.

Underlying NASA's ozone research is the knowledge that concentrations of ozone and related atmospheric constituents have changed in the past and are likely to change in the future. Changes are due to both natural and human activities, and a particular emphasis of NASA's work is the quantitative determination of present distributions and past variations. Anthropogenic changes can result from use of chlorofluorocarbons (CFCs) and related halogen-containing hydrocarbons, commercial and military aviation, and increased production of chemically and radiatively active gases such as methane and nitrous oxide. The key questions concerning atmospheric ozone facing the scientific community are thus:

- What is the global distribution of ozone in the troposphere and stratosphere and how has it changed in the recent past?
- Are the processes responsible for transport, production, and loss of trace constituents in and from the troposphere and stratosphere sufficiently well understood that predictive models for the chemical state of these regions can be developed?
- Are the current international agreements limiting the production of ozone-destroying chemicals having the expected effect on the atmospheric concentration of these species, and on ozone levels?
- What are the effects of aviation (both the current subsonic fleet and the projected subsonic and supersonic fleets), the fumigant methyl bromide, and industrially produced CFC-replacements, on the distribution of ozone and other trace constituents in the atmosphere?

- How will changing climate due to increased concentration of radiatively active trace gases affect future distributions of ozone and other chemically reactive species, such as photochemical oxidants?

In order to help answer these questions, NASA's atmospheric ozone research plan carries out several types of research:

- To characterize the global distribution of ozone, chemically active trace constituents, aerosols, and related meteorological parameters (e.g., temperature), including long-term observations of a subset of these parameters;
- To understand the processes responsible for the chemical transformations of trace constituents, the role of aerosols in affecting atmospheric chemistry, and the transport of trace constituents within the stratosphere, between different atmospheric levels (stratosphere/troposphere, stratosphere/mesosphere), and between the troposphere and the Earth's surface; and
- To quantitatively model the trace constituent composition of the troposphere/stratosphere system through the combined application of observations and global models.

The NASA research plan addresses these objectives through several program elements:

- **Laboratory Studies of Fundamental Processes**, including thermodynamic, photochemical, and spectroscopic properties of atmospheric trace constituents, covering both gas- and condensed-phase species (the latter including aerosol particles);
- **Process Studies and Field Campaigns**, involving focused measurements within a particular atmospheric region so that specific chemical and physical processes can be understood and theories can be quantitatively tested; these rely extensively on *in situ* and remote-sensing aircraft measurements, as well as ground-, balloon-, and space-based instruments;
- **Long-term Global Measurements,** including space-based measurements of ozone and other parameters, as well as ground-based measurements of concentrations of species whose concentrations affect and are affected by ozone distributions; and
- **Modeling Studies,** emphasizing global models that can be used both for retrospective data analysis and for predictive studies of the future atmosphere.

Developments which have the potential to significantly enhance NASA's abilities to investigate atmospheric chemistry and which will be incorporated into the NASA program as they become available include:

- **The launch of the Earth Observing System** beginning in 1998, especially in regards to the determination of global distributions of tropospheric ozone and its precursors for an extended period of time;
- **The availability of remotely-piloted aircraft**, which will allow for higher altitude *in situ* and remote sensing measurements than currently available from manned aircraft, as well as longer flight duration and more flexible flight trajectories; and

- **The availability of massively parallel and other high performance computing systems**, which will facilitate development and operation of more complex atmospheric chemistry models, especially three-dimensional chemistry/transport models emphasizing the troposphere and the combined effects of long-term chemical and climatic changes associated with increasing trace gas concentrations.

The development of Earth System Science means that NASA's atmospheric ozone research will also become more closely linked to the other science themes of Mission to Planet Earth (especially the long-term climate change theme) than in the past.

I. INTRODUCTION

NASA's research goals related to atmospheric ozone are to develop a detailed understanding of chemical, physical, and radiative processes affecting distributions of ozone and oxidizing species in the global troposphere and stratosphere, to accurately and precisely determine those distributions, including their spatial and temporal dependence, and to quantitatively characterize observed past and, through the use of predictive models, potential future changes in these distributions in response to specified forcings.

These goals arise from three separate but related scientific issues–each of which has broad policy implications. First, the absorption of biologically damaging ultraviolet (UV) radiation, especially in the 290-320 nm region, by ozone plays an important protective role in the Earth environment. Reductions in atmospheric ozone amounts would lead to increased flux of ultraviolet radiation at the surface, assuming other factors, such as cloudiness, remain unchanged. This would have harmful effects on plant and animal life, including human health. Second, ozone absorbs and emits radiation in several wavelength ranges, and is an important contributor to the physical state of the atmosphere and thus to the Earth's climate. Finally, ozone, together with the hydroxyl radical (OH) which is formed photochemically from ozone and water vapor, serves as a major oxidizing species in the atmosphere. Changes in ozone amounts, especially in the troposphere, will affect the lifetime of many atmospheric trace species, including both chemically active species (e.g., chlorofluorocarbon replacements) and radiatively active species (e.g., methane) and could thus have an indirect effect on their contributions to ozone depletion and climate change.

NASA's efforts are carried out in response to and in the context of federal legislation; indeed, the NASA Authorization Act and the US Clean Air Act require NASA to carry out research on stratospheric ozone and to report to Congress on a triennial basis. As scientific knowledge has evolved, recognition of the coupling between tropospheric and stratospheric chemistry has become clearer. Both must be understood if existing measurements of ozone and its future evolution are to be understood.

A particular emphasis of NASA's activities is the characterization of both natural and human-induced variations on atmospheric ozone amounts, as one cannot be understood without knowledge of the other. There have been important changes in ozone distributions, including the "Antarctic Ozone Hole" in which a significant fraction of the ozone over Antarctica is lost in the spring (especially in the lower stratosphere), much smaller reductions in ozone amounts over most of the Earth's surface (again, mainly in the lower stratosphere), and increases in ozone amounts in the upper troposphere in many, but not all, locations.

Among the human-induced variations are the effects of changing concentrations of halogen-containing species in the atmosphere. These compounds, which have been implicated in the above-noted ozone depletion, are currently subject to both domestic and international regulations (the Montreal Protocol on Substances that Deplete the Ozone Layer and its subsequent amendments and adjustments). Stratospheric chlorine levels are expected to peak at about the turn of the century and remain greater than those of today for at least a decade, meaning that (all other atmospheric parameters being equal) stratospheric ozone amounts will reach their minima during that time. Major elements of NASA's ozone efforts in the next decade are, therefore, to characterize and understand ozone distributions during this most sensitive time period. Additional elements are to assure that atmospheric halogen levels are responding as expected to legislation and to relate the observed ozone distribution to that expected based on the observed halogen distribution and other forcing factors (e.g., solar radiation) to test whether the atmosphere is behaving as expected. Underlying NASA's work is the recognition that ozone changes can only be understood in the context of a broad range of measurements of atmospheric parameters (other trace constituents, aerosols, dynamical information).

One issue of particular interest to NASA is the role of aviation in affecting the ozone distribution in the upper troposphere and lower stratosphere. This is true for both current subsonic and projected supersonic aircraft. Since major decisions about future aircraft (in particular, engine technology) will be based in part on environmental considerations, it is critical that these decisions are supported by sound scientific data and methodology.

At the surface, ozone constitutes an important pollutant, which is harmful to plant and animal life. Although urban air quality is not a NASA responsibility, NASA is concerned that the interface between air quality and global change be properly addressed, and therefore expects to pay increased attention to this coupling in the future (see Section IV.B). In this document, unless otherwise specified, the term troposphere is used to refer to the free troposphere.

In carrying out its research on atmospheric ozone, NASA fully participates in interagency and international programs and projects. It has a strong commitment to participation in, and in many cases, leadership of internationally sponsored assessments and peer-organized programs. International cooperation in space-based measurements has been significant, and will increase in importance in the future.

II. BACKGROUND

In this section, accomplishments of NASA's ozone and atmospheric chemistry research programs, the current structure of those programs within NASA, and the science questions which are being addressed now and for the foreseeable future are summarized.

A. Recent Accomplishments

Over the past decade and a half, NASA's research program, together with those of its domestic and foreign partners, has made significant progress in characterizing the distribution of ozone and other trace constituents in the atmosphere, identifying the processes which control them, and developing a suite of models which can be used both to test our understanding of the atmosphere and for predictive purposes. Particular highlights include the following:

- Demonstration that chlorine is directly involved in depletion of lower stratospheric ozone during Antarctic spring ("ozone hole" conditions);
- Recognition that the same chemical processes occur in the Arctic and Antarctic lower stratosphere during spring, and that the lack thus far of an "ozone hole" in the Arctic is due to differences in dynamics between the two hemispheres;
- Demonstration of the key role which chemical reactions occurring on the surface of aerosol and polar stratospheric cloud particles play in controlling the chemical composition of the lower stratosphere;
- Demonstration of significant isolation between wintertime polar vortices and mid-latitudes, as well as significant downward transport in these vortices over the course of the winter;
- Characterization of long-term changes in stratospheric ozone distributions, including evidence for statistically significant depletion of ozone over most of the Earth's surface, with largest changes occurring in the lower stratosphere during winter and spring;
- Determination of the global distribution of many trace constituents, including most important nitrogen-containing species and halogen reservoir species, leading to clear demonstration that stratospheric halogen atoms are of anthropogenic origin;
- Determination of long-term growth in anthropogenically-produced halogenated source gases at the Earth's surface over most of the 1980s, followed by leveling off of growth and, for most species, slow decline in the mid-1990s in response to limitations on production as required by the Montreal Protocol;
- Demonstration of consistency between burdens and changes in concentrations of halogenated source gases in the troposphere and those of halogen-containing reservoir species in the stratosphere over the course of a decade;
- Characterization of the role which major volcanic eruptions, notably El Chichon (1982) and Mt. Pinatubo (1991), play on the chemistry and dynamics of the stratosphere;
- Development of two-dimensional assessment models which are used for both retrospective data analysis and for future assessment, including calculation of atmospheric effects of projected CFC replacement molecules;
- Development of improved understanding of the effects of present and projected aviation activities on atmospheric composition, including the first ever *in situ* sampling of an aircraft plume in the stratosphere;
- Demonstration of the adequacy of current theories relating relative concentrations of photochemically active trace constituents through a combination of *in situ* measurements of concentrations with laboratory measurements of the rates of the underlying photochemical processes;
- Characterization of global distributions of tropospheric ozone and carbon monoxide using direct and/or inferred measurements, with particular recognition of spatial and temporal variability associated with biomass burning in Africa and Latin America;
- Characterization of the effect of outflow from Asian continent on the global troposphere, including determination of seasonal variation; and

- Characterization of effects of chemistry in plumes from biomass burning on distributions of ozone and other trace constituents in Atlantic free troposphere.

B. Organization of NASA's Ozone Research Effort

SCIENTIFIC RESEARCH

Ozone research within the Science Division of the OMTPE is concentrated in three research programs as well as in the Earth Observing System (EOS) Interdisciplinary Science Program, and science teams and guest investigator programs for ongoing space missions. These are:

- The Upper Atmosphere Research Program (UARP), which conducts laboratory measurements, and ground-, balloon-, and aircraft-based measurements related to the stratosphere. Some process modeling is done under UARP as well.
- The Tropospheric Chemistry Program (TCP), which emphasizes airborne field studies of the remote troposphere. As for UARP, process scale modeling is done under TCP.
- The Atmospheric Chemistry Modeling and Analysis Program (ACMAP), which emphasizes global scale chemical models of the troposphere and stratosphere, as well as the model-based analysis of trace constituent data for the troposphere and stratosphere. Studies of stratospheric dynamics are also part of ACMAP, as are large-scale modeling studies which attempt to relate atmospheric composition to processes occurring at the Earth's surface. Reprocessing and reanalysis of "old" global datasets is also carried out by ACMAP. Modeling activities supported by ACMAP play an important role in the planning, execution, and analysis phases of field experiments conducted under UARP and TCP.
- The Earth Observing System (EOS) Interdisciplinary Science (IDS) program supports two IDS efforts focusing on stratospheric chemistry. Several additional tasks focusing on the combined modeling for atmospheric chemistry and climate were selected in response to the recent augmentation of the EOS IDS program (see Section VI.A).
- The Guest Investigator Program (GIP) for NASA's Upper Atmosphere Research Satellite (UARS) and the Science Team for the Second Stratospheric Aerosol and Gas Experiment (SAGE II) instrument.

MISSION OPERATIONS AND DATA ANALYSIS (MO&DA)

The MO&DA activities are carried under the supervision of the Mission to Planet Earth (MTPE) Program Office at NASA's Goddard Space Flight Center (GSFC). MO&DA supports data analysis, algorithm development, archiving, and early-stage science validation for NASA-operating space assets, including the Total Ozone Mapping Spectrometer (TOMS), the Solar Backscatter Ultraviolet (SBUV/2), the Stratospheric Aerosol and Gas Experiment (SAGE II), the Upper Atmosphere Research Satellite (UARS), and Shuttle Solar Backscatter Ultraviolet (SSBUV) instruments. As new NASA-funded instruments begin operating, MO&DA assumes responsibility for their operation.

FLIGHT SYSTEMS

The MTPE Program Office at GSFC also supports the development of flight hardware, including pre-launch science and algorithm costs. Major systems here include the TOMS instruments, with three instruments scheduled for launch before the turn of the century (Earth Probe TOMS, launched in July, 1996, ADEOS TOMS in August, 1996; and Meteor-3M TOMS in 2000). It has begun funding of the Shuttle Ozone Limb Sounder Experiment (SOLSE) which is intended for flight on the Space Shuttle in 1997 assuming an appropriate manifest opportunity exists.

Costs for developing EOS instruments and their associated algorithms and science definition efforts are provided through the MTPE Program Office. This includes the three US (or jointly US and foreign) provided instruments on the EOS CHEM mission (launch scheduled in 2002): the Troposphere Emission Spectrometer (TES), the High Resolution Dynamics Limb Sounder (HIRDLS), and the Microwave Limb Sounder (MLS). Flight Systems Division (FSD) will also support the US team to be selected for the Japanese-provided Ozone Dynamics Ultraviolet Spectrometer (ODUS) on the EOS-CHEM platform. The Stratospheric Aerosol and Gas Experiment (SAGE III) instruments scheduled for flight in 1998 on a Russian Meteor-3M spacecraft and for the Space Station in ~2001 are also supported by the MTPE Program Office.

Future flight opportunities for atmospheric chemistry instruments may become available under the Earth System Science Pathfinder (ESSP) program and the New Millennium Program (NMP). The latter is a joint activity sponsored by MTPE and the Office of Space Access and Technology.

ATMOSPHERIC EFFECTS OF AVIATION PROJECT (AEAP)

This project is funded by the Office of Aeronautics, but is implemented in close collaboration with MTPE. AEAP efforts are responsive to two separate aeronautical programs - the High-Speed Research Program (HSRP) focusing on the development of a "next generation" supersonic transport aircraft which would be both economically viable and environmentally benign, and the Advanced Subsonic Technology Program (ASTP) which is attempting to improve various operational aspects of the current commercial subsonic fleet. The atmospheric components of HSRP and ASTP are contained within AEAP and have been designated as the Atmospheric Effects of Stratospheric Aircraft (AESA) and Subsonic Assessment (SASS) projects. The goal of AEAP is to focus and, where necessary, redirect atmospheric science investigations towards the particular atmospheric perturbations resulting from aircraft exhaust. Thus AEAP augments and in some areas extends on going activities in the core MTPE science programs related to tropospheric and stratospheric ozone. AEAP-supported tasks include laboratory studies, *in situ* field measurements, process-scale modeling, and global modeling. In addition to its focus on ozone, AEAP supports research on aerosols, clouds, and radiation, it also includes topics which are more specific to the aircraft engine environment, such as characterizing emitted species and studying changes to the exhaust gases and particles in the plumes and wakes of aircraft.

C. Current Science Questions

Many of the science questions to be addressed in the coming few years have been included in the previous section, but it is helpful to summarize them before moving onto longer-term plans, including new directions and emphases, which are expected.

These questions may be broken up into two classes: broader questions about what has happened and/or will happen, and more specific questions about what must be understood in order to develop the knowledge base needed to answer the first class of questions. Typically, the former class of questions will involve the construction of extended datasets and/or computational models, while the second set will involve the detailed understanding of relevant processes.

Key current science questions include but are not limited to the following:

1. STRATOSPHERIC OZONE

a. Broad Questions

- Can we understand the tropical and mid-latitude changes in total ozone and in its vertical distribution over the last 15 years, including the quantitative assignment of the origin of these changes to chemical and dynamical processes?
- Can we quantitatively explain the interannual variability in the strength, size, and persistence, of the Antarctic ozone hole?
- Can we demonstrate that both surface and stratospheric concentrations of halogen-containing species are behaving as expected in response to international agreements restricting their use as well as known sources and loss properties of the species?
- Can we accurately simulate how the atmosphere responds to large volcanic eruptions, including both past (e.g., the El Chichon and Mt. Pinatubo eruptions) and any future eruptions?
- Can we accurately predict perturbations to ozone distributions which would be caused by future aircraft operations, especially supersonic civil transport aircraft, as well as potential future industrial chemicals?
- Can we accurately predict how the thermal and dynamical properties, and through them the chemical properties, of the stratosphere will change in response to increasing concentrations of radiatively active gases?

b. Process Questions

- Can we quantify transport of trace constituents across atmospheric barriers, including the tropical/mid-latitude barrier, the mid-latitude/polar vortex barrier, and also across the tropopause?
- Can we refine our knowledge of the roles which halogen-containing species play in the stratosphere, including reactions which repartition chlorine and bromine among their various compounds, and the reactions of iodine-containing species in the lower stratosphere?
- Can we improve our understanding of the characteristics and formation properties of particles in polar stratospheric clouds and aerosols throughout the stratosphere?

- Can we understand the relative importance of the various cycles for ozone production and loss throughout the stratosphere, particularly at altitudes where the chemistry transitions from heterogeneous to homogeneous control?

2. TROPOSPHERIC OZONE

a. Broad Questions

- Can we characterize and understand the record of changes in ozone profiles in the free troposphere, including spatial and temporal variability?
- Can we quantitatively determine the atmospheric lifetimes of hydrogen-containing species such as methane and HCFCs and understand how these may change as the trace constituent composition and dynamical properties (e.g., temperature, moisture) of the atmosphere change?
- Can we determine what role, if any, subsonic aircraft operations have had on tropospheric trace constituent distributions, and what effect future operations of increased numbers of aircraft might have?
- Can we predict what changes in surface production of chemically active trace constituents such as nitrogen oxides, methane, carbon monoxide, and non-methane hydrocarbons will have on the composition of the global troposphere?
- Can we better determine the distribution of tropospheric ozone through application of current space-based remote sensing techniques, as well as those projected for the future?
- Can we estimate the net processing effect of clouds on the trace constituent distribution of the upper troposphere?
- Can we quantify the impact of stratospheric changes (e.g., ozone depletion) on tropospheric chemistry, especially that due to increased penetration of ultraviolet radiation?
- Can we improve our understanding of the budgets of biogenic organic and inorganic trace species that play major roles on tropospheric ozone, including isoprene, CO, CH_4, and methyl halides?

b. Process Questions

- Can we quantitatively understand the contributions of different sources to ozone distributions in the remote troposphere, including the relative contributions of outflow from developed regions, biomass burning, *in situ* production, and downward transport from the stratosphere?
- Can we quantify the sources of total reactive nitrogen in the upper troposphere, including the spatial and temporal dependence of contributions from *in situ* emission by aircraft, *in situ* production by lightning, downward transport from the stratosphere, and upward transport of species emitted at the surface?
- Can we improve our knowledge of the distributions of reactive nitrogen compounds in the troposphere through improved measurements and models so that current discrepancies between observations and model calculations can be resolved?
- Can we determine what role chemical processes occurring on dust and aerosol particles, as well as in clouds, and wet/dry deposition at the surface, play on the trace constituent composition of the global troposphere?

- Can we determine what role, if any, halogen species play in the chemistry of the global lower troposphere?
- Can we accurately characterize the processes by which naturally and anthropogenically produced sulfur-containing species are oxidized in the atmosphere to sulfuric acid and thus contribute to aerosol formation and/or growth?

III. ELEMENTS OF NASA'S OZONE PROGRAM

NASA's ozone research can be divided into six categories, with close interaction between each of them. NASA strives to maintain a balanced program among these areas, including consideration of both short- and long-term horizons, and strives to maintain sufficient flexibility that it can deal with new scientific issues as they arise. The following section briefly describes the work in each of these areas. Present and future measurement capabilities for different atmospheric trace constituents are summarized in Table 1.

A. Laboratory Science

Laboratory measurements of fundamental physical and chemical problems may be thought of as coming in three separate areas. First, laboratory measurements of rates of chemical kinetic and photochemical processes, are carried out to support understanding of atmospheric transformations and for inclusion in computational models, including detailed process models and global atmospheric chemical models. In recent years, much of this activity has centered on chemistry and spectroscopy of halogen-containing molecules, including oxides and other compounds, of chlorine, bromine, and, most recently, iodine. Processes which lead to ozone production in the troposphere have also been studied. Results of laboratory measurements are critically evaluated in the *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling* report, which is published biennially and represents the community consensus of reaction rates, cross sections, and quantum yields. The laboratory techniques may be applied to help determine the atmospheric lifetimes of potential future industrial chemicals which may impact the ozone layer or atmospheric radiative forcing.

Second, spectroscopic measurements (and some related photochemical phenomena) are made to support NASA's remote sensing efforts, including those for ground-, balloon-, aircraft-, and space-based platforms. Particular areas of emphasis include spectroscopy of polyatomic molecules at the temperature and pressure conditions appropriate to the stratosphere and upper troposphere, which will be needed to fully utilize observations made by the EOS HIRDLS, TES, MLS, and SAGE III instruments, and photochemical and spectroscopic parameters needed for the interpretation of lidar measurements made both from the ground and from aircraft.

Finally, thermodynamic properties and associated kinetic information on atmospheric aerosol and stratospheric cloud particles are studied. Attention has been focused on the three-component system water-nitric acid-sulfuric acid under stratospheric conditions. Continued emphasis on this area is called for, as there are outstanding questions about the identity of particles present in polar stratospheric clouds and lower stratospheric/upper tropospheric aerosols as well as the detailed mechanism by which they form. There is also appreciable work remaining on the physical and chemical properties of stratospheric sulfate aerosol particles and ternary liquid droplets. Longer-

term efforts are needed to characterize the properties and impacts of soot particles in the atmosphere and optical properties of aerosols in order to evaluate the feasibility of using infrared remote sensing techniques for the determination of aerosol composition and density.

B. Ground-Based Measurements

NASA's ground-based measurements center on the use of globally-distributed high-quality research instruments for the determination of long-term changes in atmospheric trace constituent variability. The two major efforts in this area are the AGAGE (Advanced Global Atmospheric Gases Experiment, formerly the ALE-GAGE - Atmospheric Lifetime Experiment - Global Atmospheric Gases Experiment) and the Network for the Detection of Stratospheric Change (NDSC). These programs provide critical monitoring of the surface concentrations of both anthropogenically and biogenically produced trace gases (AGAGE) and of the chemical composition of the lower stratosphere (NDSC).

AGAGE uses gas chromatography and gas chromatography coupled with mass spectrometry to measure with high frequency the concentration of naturally and anthropogenically-produced atmospheric gases at the Earth's surface. AGAGE stations are shown in Figure 1. The emphasis in AGAGE is on halogen-containing species (although nitrous oxide and methane are measured), with its original focus on chlorinated species having been expanded to bromine-containing species like halons and methyl bromide, as well as HCFCs. AGAGE investigators have a significant modeling program to ensure that their full global data set is exploited.

NDSC is an internationally directed and sponsored program (major support from NASA, NOAA, and foreign partners) in which a number of remote-sensing instruments meeting mutually-agreed upon standards are deployed at sites around the world. Major instrument categories deployed at the NDSC's "primary sites" include Fourier transform interferometers, millimeter wave emission spectrometers, visible/UV absorption spectrometers, and lidars; together these provide measurements of column amounts and/or profiles of atmospherically important species. In addition to the primary NDSC sites, complementary sites involving a less complete set of instruments are also participating. Primary NDSC sites and a summary of complementary sites are also given in Figure 1. Since consistency of calibration, both across instruments and over long time periods, is a hallmark of the NDSC program, there will be a continuing program of instrument comparisons through laboratory and field efforts. NDSC has a program for associated modeling investigations to help ensure that data will be fully utilized. NDSC instruments have also been involved in validation measurements for space-based instruments, and provide measurements in support of aircraft campaigns.

C. Balloon-Based Measurements

NASA has a long heritage of using balloons to measure the trace constituent composition of the middle atmosphere. There are three major applications of the balloon program. First, balloons provide a unique way of covering a broad range of altitudes for *in situ* (or remote sensing) measurements in the stratosphere. Of particular interest is the 22-40 km region which is above the altitude range of current airborne platforms such as the ER-2. In some cases, a combination of instruments on a single balloon gondola can provide a complete measurements set which can be utilized together with process models to carry out detailed tests of photochemical theory. A balloon

component, known as Observation of the Middle Stratosphere (OMS), is planned in association with the transport-focused STRAT series of ER-2 missions (see below).

Second, balloon instruments provide the opportunity for correlative data for space-based measurements, including both validation ("atmospheric truth") and complementary data (for example, measurement of species not measured from the space-based instrument). Balloon instruments formed a critical part of the correlative measurements program for the Upper Atmosphere Research Satellite (UARS), and current plans are to use some of NASA's balloon instruments in support of the validation program of the Japanese ADEOS satellite (launch scheduled summer, 1996) and the European ENVISAT (launch scheduled in 1999).

Finally, balloon-based platforms constitute important venues for testing instruments under development. These can be either potential instruments for uncrewed aerial vehicles (UAVs) or, in some cases, for space-based remote sensing instruments.

D. Aircraft-Based Measurements

Aircraft-based measurements for tropospheric ozone have recently centered on use of the NASA DC-8 aircraft for measurements of ozone, other trace constituents, and meteorological parameters in the remote troposphere. This aircraft includes both *in situ* instruments and an ozone/aerosol lidar for remote sensing (both above and below the aircraft). A map showing the geographical distribution of tropospheric chemistry aircraft missions is given in Figure 2. The focus of these missions has been the remote troposphere in order to define the tropospheric background and to look at effects of human activities which influence the troposphere on a regional-to-global scale. Such activities include biomass burning from South America and Africa and the large continental outflow of pollution from North America and Asia. The next major tropospheric aircraft campaign will be in the central Pacific Ocean area in July-September 1996 (Pacific Exploratory Mission—Tropics, or PEM-Tropics). This mission will include both the DC-8 and P-3 aircraft. This will be followed by the Global Tropospheric Experiment/Transport and Atmospheric Chemistry Experiment (GTE/TRACE B) mission to Brazil in February-April 1999. This will be done as part of a coordinated NASA-field study in Brazil addressing surface-oriented climate, ecology, and biogeochemistry. The subsequent GTE aircraft mission, whose exact nature has not yet been determined, is tentatively scheduled for 2001. In the time between PEM-Tropics and GTE/TRACE-B, there will likely be an aircraft intercomparison, focusing on OH and NO_x measurements.

Stratospheric aircraft campaigns involve both the ER-2 and DC-8. Over the past decade, campaigns emphasized high latitudes in both the Northern and Southern Hemisphere (Airborne Antarctic Ozone Experiment—AAOE in 1987, first Airborne Arctic Stratospheric Expedition—AASE I in 1988-89; second Airborne Arctic Stratospheric Expedition—AASE II - in 1991-92; and the recently-completed Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft—ASHOE/MAESA). The more recent campaigns have also focused on the mid-latitudes (Stratospheric Photochemistry, Aerosol, and Dynamics Expedition—SPADE campaign) and the tropics (ASHOE /MAESA). The aircraft campaigns support both the basic science objectives of UARP and the more applied needs of AEAP. During ASHOE/MAESA, for instance, the ER-2 was able to sample the plume of a Concorde flying near New Zealand.

The current ER-2 payload provides *in situ* measurements of nearly all important trace constituents in the lower stratosphere, including the important radical species OH, HO_2, NO, NO_2, ClO, and BrO. Together with measurements of source and reservoir gases, this payload provides for critical tests of photochemical models in the lower stratosphere. A representation of the latitudinal coverage of past, present, and future stratospheric aircraft missions is given in Figure 3.

Most recent aircraft campaigns include the recently initiated Stratospheric Tracers of Atmospheric Transport (STRAT) campaign, a 3-year (1995-1997) multi-deployment ER-2 campaign focusing on transport of long-lived trace gases in the lower stratosphere, and the Vortex Ozone Transport Experiment/Tropical Ozone Transport Experiment (VOTE/TOTE) mission, which used the DC-8, equipped for both remote sensing and *in situ* observations, to focus on transport across the winter polar vortex/mid-latitude and the subtropical barrier, respectively. In particular, VOTE/TOTE inaugurated the use of a newly-developed methane/water vapor/temperature lidar system, which complemented the existing ozone/aerosol lidar by providing simultaneous information on dynamically controlled constituents. During operations of these missions, there was an opportunity for the ER-2 to sample the DC-8 plume.

A focused ER-2 chemistry experiment, known as Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) is planned for the spring and summer of 1997 to provide the first summer-time measurements in the northern mid-high latitude stratosphere. This mission, to be based in Fairbanks, Alaska, will consist of three three-week deployments, and will emphasize detailed chemistry observations. A balloon campaign (see Section III.C) may be implemented as part of POLARIS.

A new chlorine nitrate *in situ* instrument is expected to be ready for the late 1996 ER-2 deployment as part of the STRAT campaign. This continues the improvement of ER-2 instruments. New ER-2 instruments introduced in the past few years include a lidar for remote sensing measurements of tropospheric water vapor, aerosols, and clouds, as well as *in situ* instruments for measuring H_2O_2, OH, HO_2, CO_2, UV radiation, CFCs and numerous other halogen and hydrogen-containing species, and N_2O, SF_6, CH_4, CO, HCl, and NO_2. New DC-8 instruments include improved lidar instruments, including those for tropospheric and stratospheric ozone and aerosols, clouds, and tropospheric water vapor, and fast response *in situ* measurement for trace gases such as O_3, CH_4, and CO.

The Subsonic Assessment Program of the Atmospheric Effects of Aviation Project will be sponsoring dedicated use of airborne platforms to support its objectives. A DC-8 based campaign, SASS Ozone and Nitrogen Oxide Experiment (SONEX), to investigate the sources and chemistry of upper tropospheric and lower stratospheric NO_x (NO_x = NO + NO_2) and its role in ozone formation is planned for the summer of 1997. The SONEX campaign will include measurements both inside and outside the heavily trafficked North Atlantic flight corridor to try to help asses the contribution of emissions from currently-operating subsonic aircraft to the budgets of ozone and NO_x in these regions. SASS is also planning to initiate support for development of a single integrated instrument package designed for simple and economical use aboard commercial aircraft.

This package would help generate a spatially and temporally extensive measurement set for key tracers of atmospheric transport in the troposphere and lower stratosphere, and would likely include one or more tracers with surface sources and simple atmospheric chemistry, one with seasonally-varying sources and/or more complex atmospheric chemistry, a stratospheric tracer, and water vapor. Proposals in both these areas have recently been requested under a NASA Research Announcement issued for AEAP/SASS (NRA-96-OA-01).

In 1998 and beyond, there will quite likely be a series of aircraft flights as part of the validation program for EOS instruments (see following section). The first atmospheric chemistry instruments to be launched include the Measurement of Pollution in the Troposphere (MOPITT) and the Stratospheric Aerosol and Gas Experiment (SAGE III) instruments. Aircraft campaigns using an airborne version of MOPITT, as well as *in situ* sampling instruments for both CO and CH_4, are planned. Since SAGE III makes measurements in both the troposphere and stratosphere, aircraft campaigns involving aircraft capable of flying in both regions of the atmosphere are planned. The solar occultations for the SAGE III instrument all take place at high latitudes, and the aircraft validation campaigns in support of SAGE III will probably emphasize the high latitude Northern Hemisphere.

The atmospheric aircraft campaigns, especially the stratospherically-oriented ones, are closely tied in with MTPE's modeling and satellite programs. Modeling groups play a significant role in the aircraft campaigns. Most missions have "theory teams" designated as part of the overall science teams, and individuals associated with them participate intimately in the planning, operation, and data analysis of the missions. Satellite data are involved in several ways. Data from NASA's TOMS instrument have been most extensively used in order to help with flight planning in both the tropospheric and stratospheric campaigns, and global meteorological data (including assimilated data) are also used in this way.

In the longer-term, uncrewed aerial vehicles (UAVs) are expected to play a significant role in the atmospheric chemistry programs. UAVs are likely to have the capability to fly higher in the stratosphere than the ER-2, and may also be able to fly longer (both in terms of time and distance) which would facilitate types of flight paths not possible with current aircraft. MTPE has recently agreed to support an effort to prepare a payload for a UAV (Perseus B) which would measure the radiation field in the tropopause region together with the concentration of several radiatively active trace species (notably O_3 and H_2O). Instrument development for UAVs has also begun (see Section IV.B.1).

E. Space-Based Measurements

The best known parts of NASA's space-based measurement program for ozone are the long-term ones which have been useful in characterizing the global aspects of ozone distribution and of long-term changes over more than 15 years. There are three such instrument sets: the Total Ozone Mapping Spectrometer (TOMS), the Solar Backscatter Ultraviolet (SBUV) series (done in conjunction with NOAA), and the Stratospheric Aerosol and Gas Experiment (SAGE) series. NASA (and, in the case of SBUV/2, NOAA) will continue operation of these instruments throughout the decade with a minimum (or, if launch schedules and instrument lifetimes permit, an absence) of data gaps. Operation of these instruments will be accompanied by continuing calibration, validation, and data analysis efforts in order to ensure that these critical instruments are

returning data which is useful for trend studies (typically precision of 1 percent/decade, which imposes constraints on absolute accuracy and long-term stability of instruments). As part of the calibration and validation process, periodic reprocessing of datasets is likely, and NASA will need to maintain sufficient capabilities so that these can be accomplished. The next generation SAGE instrument which will have a lunar occultation mode as well as the solar occultation mode of SAGE II, along with increased spectral resolution, number of channels, and instrument sensitivity and dynamic range. Earth Probe TOMS was launched on 2 July 1996, and future launch dates are August 1996 for ADEOS TOMS, and 2000 for Meteor-3M TOMS, approximately 1998, 2000, and 2003 for SBUV/2, and 1998 and approximately 2001 for SAGE III.

The Upper Atmosphere Research Satellite (UARS) will continue to be operated as long as the spacecraft and instruments so warrant. The spacecraft has already exceeded its design life, and plans are now focused on continuing measurements for a long time period. This will likely involve restricting operation of some instruments which have already begun to have problems or are thought to be less critical for extended operation, especially now that UARS is forced to operate in a "reduced power" mode. In particular, operation of the HALOE instrument, which provides measurements of profiles of ozone and other important gases, notably the halogen reservoir species hydrogen chloride (HCl) and hydrogen fluoride (HF), use of the MLS instrument for measurement of stratospheric ClO, HNO_3, and O_3, as well as upper tropospheric H_2O, and the solar measuring instruments (Solar Ultraviolet Spectral Irradiance Monitor and Solar Stellar Intercomparison Instrument for spectrally-resolved UV radiation and the Active Cavity Radiometer Irradiance Monitor for total solar irradiance), will continue for as long as possible.

NASA is making limited use of the Space Shuttle for atmospheric chemistry measurements. The Shuttle Solar Backscatter Ultraviolet (SSBUV) instrument made its last planned flight STS-72, launched 11 January 1996. NASA is sponsoring the German Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere—Shuttle Pallet Satellite (CRISTA-SPAS) payload for a shuttle flight in summer 1997. The CRISTA-SPAS, together with its companion instrument, the Middle Atmosphere High-Resolution Spectrographic Investigation (MAHRSI) instrument, provide unique data in several areas, including small-scale dynamical variability in trace constituent composition (CRISTA), and measurements of hydroxyl in the upper and middle stratosphere (although the ability of MAHRSI to measure OH in the middle stratosphere has yet to be quantitatively demonstrated). The Shuttle Ozone Limb Sounder Experiment (SOLSE) is currently under development at the Goddard Space Flight Center; this would function as a "proof-of-concept" for an ultraviolet limb sounder, which is a potential "next generation" ozone profiling instrument. A flight opportunity for SOLSE (preferably the same flight as CRISTA/MAHRSI) has been requested.

Tropospheric carbon monoxide measurements will be made with some vertical profile information (4 levels) from the MOPITT instrument scheduled for launch aboard the first EOS spacecraft (EOS AM) in 1998. Additional space-based measurements of CO will be made from the MicroMAPS instrument on the Clark spacecraft, scheduled for launch in the second half of 1996, and the "MAPS on MIR" mission, which is scheduled for launch in January 1997. The former will measure CO distributions at three pressure levels in the troposphere over the latitude range from 82 degrees north to south for a period of at least one year, while the latter will make measurements over the latitude range from 53 degrees north to south for a 3-6 month period. The MOPITT instrument will also measure total column methane.

The chemistry (CHEM) platform of the Earth Observing System, to be launched in 2002, will have four complementary instruments which utilize different wavelength regions and viewing techniques to measure ozone and related atmospheric constituents. Three will focus on the stratosphere—the High-Resolution Dynamics Limb Sounder (HIRDLS), an infrared emission spectrometer which will also measure small-scale dynamical variability in trace constituent distributions, the Microwave Limb Sounder (MLS), which will measure concentrations of many radical and reservoir species, and the Japanese-provided Ozone Dynamics Ultraviolet Spectrometer (ODUS), a "next-generation" TOMS-like instrument which will provide daily maps of total ozone. The remaining instrument, the Tropospheric Emission Spectrometer (TES), will measure profiles of ozone and several other important constituents in the troposphere, and will also measure a number of species in the lower stratosphere. HIRDLS and MLS are designed to provide information on the upper troposphere as well as the stratosphere. There have been numerous discussions about possible changes to the CHEM mission, including modifications to one or more instruments, and the exact payload arrangements and schedule for this mission are subject to change.

The SAGE III instrument is slated for flight aboard a Russian Meteor-3M spacecraft in 1998 and the International Space Station in approximately 2001. These are in complementary orbits—the polar sun-synchronous orbit of Meteor-3M will put the SAGE solar occultations at high latitudes, while the inclined orbit (51.5°) of Space-Station will provide solar occultation coverage from the tropics to approximately 65° latitude. Lunar occultations will cover a broad range of latitudes, and will provide the opportunity for measurements of NO_3 and OClO, which are only present in significant amounts at nighttime due to their rapid photolysis during the day.

Additional instrument concepts are being considered by NASA investigators for possible space flight, and may be proposed in response to the Earth System science Pathfinder announcement released in the summer of 1996.

In addition to its emphasis on present and future spacecraft, NASA also supports analysis, interpretation, and in several cases, reprocessing of historic space-based datasets. These efforts are focused to allow for more direct comparisons of older measurements with newer ones, in spite of differences in instrument or technique. Several examples of these efforts are underway, including reprocessing of Limb Infrared Monitor of the Stratosphere (LIMS) data from Nimbus 7 (data from 10/78-5/79) to provide optimal comparisons with data from infrared instruments on UARS, and reanalysis of BUV data from Nimbus 4 (early 1970s) and Selective Chopper Radiometer data (mid-1970s) for comparison with TOMS data, especially over Antarctica. Studies are also being carried out to extend profiles of trace constituents measured by the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument during its four Shuttle flights into the middle and upper troposphere, as well as to further refine its measurements of concentration profiles of some 30 stratospheric species.

NASA is also beginning a closer cooperation with NOAA concerning the possible development of ozone-measuring instruments for the NPOESS in which DOD, NOAA, and NASA have been directed to combine their operational measurements into a single suite. The major need in this area is to find a replacement for the SBUV/2 instrument, which suffers from numerous limitations, including low vertical resolution and an inability to measure the ozone profile below the peak in the ozone layer. The replacement instrument (or instruments) should have capability for both total ozone and ozone vertical profile measurements, with improved vertical resolution and measurement capability in the lower stratosphere.

F. Modeling and Data Analysis

Models play an important role in NASA's atmospheric chemistry efforts. Models are used both to provide a means to test our understanding of processes affecting the distribution of ozone and other trace constituents and of the past evolution of these distributions, as well as for forecasting the future evolution of the atmosphere based on prescribed scenarios. Global models are a particular focus of these efforts both because of the global nature of the atmosphere and the processes controlling its trace constituent distribution, and because of the significant amount of global data NASA produces through its measurement programs. Development and evaluation of these models requires the availability of fundamental data on atmospheric processes (see Section III.A) as well as atmospheric measurements (Sections III.B–III.E).

NASA's modeling and data analysis efforts have been closely tied to the assessment effort, notably the WMO/UNEP ozone assessments and also the IPCC climate assessment. The NASA modeling community also participates in the AEAP assessments of atmospheric effects of aviation (1995 supersonic aircraft assessment underway, preliminary subsonic aircraft assessment planned for 1996). Model intercomparisons (including both model-model and model-data) are typically done in conjunction with the assessment efforts. A summary of past, present, and potential future model intercomparisons and assessment applications is given in Figure 4.

The smallest-scale type of modeling carried out typically attempts to explain multiple observations in a narrow range of time and/or space. Photochemical box models and parcel trajectory models form the backbone of these process modeling activities. There is a strong synergy between laboratory science, field observations, and process-scale modeling. Process models can also lead to improved parameterizations which can be put into global models.

Global datasets are interpreted in light of calculations made with two- and three-dimensional global chemistry/transport models and statistically-oriented data analysis. The spatial and temporal dependence of ozone related to forcing factors such as the 11-year solar cycle, the quasi-biennial oscillation, and long-term change in atmospheric trace constituent composition are best examined with multi-dimensional models.

NASA supports some regional scale modeling efforts, especially in tropospheric chemistry. NASA-sponsored work in this area typically focuses on those regions where the tropospheric chemistry aircraft missions have been flown, such as the East Asian area of the two PEM missions flown to date (PEM WEST A, PEM WEST B), and the South America-Africa regions sampled by the Transport and Atmospheric Chemistry Near the Equator—Atlantic (TRACE-A). Some regional models also emphasize issues such as convective transport of trace gases and cross-tropopause transport associated with tropopause folds.

The major part of NASA's modeling effort is in global two- and three-dimensional atmospheric chemical models. A hierarchy of atmospheric chemical models is given in Figure 5. Two-dimensional (2-D) models have formed the backbone of the assessment modeling effort for the stratosphere. Particular interest lies in the development of "interactive" 2-D models which attempt to simulate the combined dynamical, radiative, and chemical response of the atmosphere to

changes. Such models, although suffering from limitations inherent in 2-D models, may be especially useful in contributing to long-term assessments where agents of climate change (e.g., increased carbon dioxide) will lead to changed atmospheric temperature fields and resulting dynamical ones.

The importance of three-dimensional (3-D) models will increase in the future. This is particularly true for tropospheric chemistry, where there is strong longitudinal and temporal variability in species such as the oxides of nitrogen and ozone. Aviation-related issues, including those for both subsonic and supersonic aircraft, also indicate the use of 3-D models. Three-dimensional chemistry/transport models will use wind fields from general circulation models and data assimilation systems. While most of the past activity in 3-D chemical modeling has been run "off-line" wherein the chemical constituent distributions do not affect the dynamics, it is likely that in the next few years, chemistry-transport studies will be done "on-line."

A major lesson of the last decade has been the important roles of aerosol and cloud particles in controlling the trace constituent distribution of the stratosphere, and model development in the future will emphasize appropriate treatment of particles and their interaction with chemistry (and, where needed, radiation). In particular, aerosol/cloud microphysical models will likely need to be incorporated into 3-D models, which will place further strain on computational resources. The presence and effects of aerosols, clouds, and dust particles in global tropospheric models must also be considered for future inclusion.

IV. LINKS TO OTHER NASA ACTIVITIES

A. Other Research Foci within MTPE

NASA's efforts in atmospheric ozone and chemistry have some overlap with the other research foci currently underway within MTPE. Several of these relationships have been mentioned in the text, so these are briefly summarized here:

1. SEASONAL-TO-INTERANNUAL CLIMATE VARIABILITY

Much of NASA's efforts in stratospheric chemistry are to understand the evolution of ozone over the recent past (during which there have been good global or near-global observations of total ozone using space- and/or ground-based measurements). This ties in with NASA's interests in studies of seasonal-to-interannual variability in climate. Changes in atmospheric ozone can only be understood in the context of changes in temperature, and processes which affect the thermal structure of the surface-atmosphere system, such as the El Niño Southern Oscillation and the Quasi-Biennial Oscillation. These have been shown to have a measurable effect on the distribution of atmospheric ozone. Volcanic eruptions similarly perturb both the chemical and dynamical state of the atmosphere. The stratosphere may provide a significant downward forcing on the troposphere, especially as it is forced by the 11-year solar cycle through the absorption of short wavelength ultraviolet light by ozone. Finally, data assimilation procedures, which have been used almost exclusively for meteorological parameters, are now beginning to be used for chemical constituents (see Section VI.B).

2. Long-Term Climate Variability

The development of research and assessment models which can simulate the long-term changes in concentrations of ozone, aerosols, and other radiatively active species in the atmosphere is an important part of NASA's atmospheric chemistry research program. These models must correctly account for changes in climate due to changing trace gas concentrations and/or land use patterns. In turn, distributions of radiatively active species are needed as input for climate models. Ultimately, a suite of coupled models, which account for changes in both chemical and thermal properties of the atmosphere, must be developed. In the interim, models which do not fully represent the range of couplings are used.

3. Land Cover Change

Tropospheric concentrations of biologically-produced trace gases, such as methane, carbon monoxide, nitrous oxide, and methyl bromide, will depend on the rates by which they are emitted by vegetation, industry, and other human activities at the Earth's surface. Changes in land use patterns can therefore affect trace constituent distributions in the atmosphere. This input is needed, both for understanding past trends in trace gases, and in forecasting future trends. Similarly, vegetated land surfaces may constitute a sink for trace gases and any changes in surface loss rates in both the past and future are needed for models to accurately represent the loss of trace constituents. Ultimately, interactive models which couple the atmosphere and the biosphere are needed.

4. Natural Hazards

Since sulfur dioxide and ash are important products of volcanic eruptions, measurements of these products in the atmosphere following eruptions are important. They not only help shed light on the magnitude and characteristics of the eruption, but they are needed to help understand how the chemical and thermal state of the atmosphere may be altered following eruptions. These measurements can be made in essentially real-time by the TOMS instrument, and can be used operationally (see Section VI.F)

B. Other Strategic Enterprises within NASA

1. Aeronautics Enterprise

The close collaboration between MTPE and the Office of Aeronautics through its Atmospheric Effects of Aviation Project (AEAP), which studies the effects of subsonic and supersonic aircraft on atmospheric chemical composition and radiative properties, have been discussed already (see Section II). An additional overlap has been through the Environmental Research Aircraft and Sensor Technology (ERAST) program. In addition to supporting the development of remotely piloted aircraft, which are expected to have great utility in the study of both tropospheric and stratospheric chemistry, the ERAST program has supported the development of six new *in situ* instruments for ultimate use on UAVs. In the interim these instruments may be used on the NASA ER-2, the NCAR WB-57F, and/or balloons as part of UARP- and AEAP-sponsored field programs.

2. Scientific Research Enterprise

There is significant science overlap between MTPE science and that in the areas of Space Physics and Planetary Atmospheres. Interaction with the Space Physics Division centers on thermospheric and mesospheric science. Significant data on those regions of the atmosphere, as well as on the spectral output of the sun, have been obtained from MTPE-sponsored missions, including UARS and the ATLAS series of shuttle flights. The UARS GIP includes support for several teams emphasizing mesospheric, thermospheric, and solar science. The planetary atmospheres program in the Solar System Exploration Division conducts laboratory studies of photochemical and spectroscopic processes relevant to planetary atmospheres, and these studies closely parallel those supported by MTPE for the Earth's atmosphere. Finally, MTPE coordinates with the Office of Space Science in the organization of balloon campaigns so that deployment costs can be minimized.

3. Space Technology Enterprise

The closest interaction between MTPE and the Space Technology Enterprise will come through the New Millennium Program, in which the development of potential space-based instruments for studying the Earth will be developed. A number of candidate instrument concepts (and instrument/platform combinations) which could be used for the study of atmospheric chemistry are under consideration. There is also a tie through the Clark spacecraft, which will carry a small carbon monoxide-measuring instrument (MicroMAPS).

4. Human Exploration and Development of Space Enterprise

A small number of atmospheric chemistry measuring instruments will be flying on manned space platforms in coming years. The last planned flight of the SSBUV instrument was on the STS-72 flight in January 1996, and the CRISTA/SPAS and MAHRSI instruments will fly on the Shuttle in 1997. In the longer-term, the SAGE III instrument will be accommodated on the International Space Station. The MAPS instrument previously used on the Space Shuttle is to fly on the Russian MIR space station, and the Russian-German MIRIAM/DOPI instrument is likely to become an official part of the joint US-Russian science program for the MIR platform.

V. LINKS TO OTHER ORGANIZATIONS AND PROGRAMS

NASA's research effort on ozone and atmospheric chemistry is closely tied in with that of other agencies of the federal government, that of foreign governments and organizations, as well as peer-led international scientific planning groups. In this section, those relationships are briefly summarized.

A. Other US Government Agencies

Coordination of research efforts on ozone and atmospheric chemistry are carried out through a number of groups, including the Stratospheric Monitoring subgroup of the Office of the Federal Coordinator for Meteorological Services and Supporting Research (which NASA co-chairs with NOAA), the interagency working group on UV monitoring, and the Air Quality Research Subcommittee of the Committee on the Environment and Natural Resources.

Direct collaboration with other US agencies includes the following:

1. National Oceanic and Atmospheric Administration

NASA's closest tie in atmospheric chemistry research has historically been with NOAA. In particular, the Aeronomy Laboratory and the Climate Monitoring and Diagnostics Laboratory of NOAA's Environmental Research Laboratories have been active participants in both the tropospheric and stratospheric aircraft experiments. They have contributed several critical instruments to the ER-2 for the stratospheric aircraft missions, and will be providing one for the OMS balloon campaign. Aeronomy lab personnel have served on the theory team for these missions, and served as project scientist for the AAOE, AASE I, and ASHOE/MAESA (as well as the upcoming POLARIS) missions. They have also provided crucial laboratory measurements on photochemistry, spectroscopy, and thermodynamics or key atmospheric trace constituents. The WMO/UNEP assessments have historically involved close interaction between NASA and NOAA. NASA also cooperates closely with the National Environmental Satellite Data and Information Service (NESDIS) in the development of algorithms, calibration, quality control, and validation for the SBUV/2 instruments which fly aboard the operational NOAA meteorological satellites. NASA's SSBUV program has played a particularly important role in maintaining the calibration of the SBUV/2 instruments (both individually and as a series). NASA scientists collaborate closely with those from the National Meteorological Center for Environmental Protection (NCEP) in studies of stratospheric temperatures and ozone distributions. Currently, NASA and NOAA personnel are engaged in discussions concerning possible ozone-measuring instruments to fly as part of the National Polar Orbiting Environmental Satellite System (NPOESS).

2. National Science Foundation

Closest interactions with NSF involve the National Center for Atmospheric Research (NCAR), which also provides aircraft instruments for the ER-2 and DC-8. NCAR participates in a variety of MTPE-sponsored modeling and data analysis efforts, including the UARS GIP and, most recently, the SAGE II Science Team. The NCAR atmospheric chemistry modeling group plays a critical role in the core model being developed by AEAP together with ACMAP.

3. National Institutes for Standards and Technology

NIST laboratory scientists play a significant role in carrying out laboratory measurements of atmospheric spectroscopic and photochemical processes, and also participate extensively in the biennial revision of the *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling* report.

4. Department of Defense

Close interaction is being developed with the Naval Research Laboratory (NRL), through its current flight of the Polar Ozone Aerosol Monitor (POAM) instrument and its planned follow-ons, including those for an inclined orbit (OOAM, 1997-98), and a polar orbit (POAM III, 1997-98). NRL also provides the SUSIM instrument on UARS (and ATLAS), as well as the MAHRSI instrument which flies on the Space Shuttle as part of the CRISTA/SPAS payload. NRL scientists are also active in developing coupled two-dimensional models of the stratosphere and mesosphere, and closely interact with more stratospherically-oriented modelers, especially at the Goddard Space Flight Center. NASA will also be collaborating with DOD supported scientists at the Johns Hopkins University Applied Physics Laboratory associated with the Midcourse Space Experiment (MSX) launched in the spring of 1996. In particular, there is an ultraviolet instrument (UVISI) aboard MSX that will serve to demonstrate potential new technology which could be useful in a future class of ozone-measuring instruments.

5. Environmental Protection Agency

EPA and NASA interact on a regular basis to ensure that NASA's efforts on stratospheric ozone are useful to policy makers and that scenarios used by NASA's modelers for both past and future emissions of CFCs and related molecules are accurate. EPA (together with DOE and NOAA) provides leadership for NARSTO, to which NASA is a signatory agency.

6. Department of Energy

DOE, through its atmospheric chemistry program, has significant overlap with NASA. DOE recently inaugurated its own atmospheric ozone program, including among other activities a reanalysis of SAGE data. The Lawrence Livermore National Laboratory is serving as the host institution for the Core assessment model being developed by AEAP with ACMAP participation.

B. International Bodies

NASA's modeling activities are closely coordinated with their foreign counterparts. Much of this cooperation has been carried out as part of the WMO/UNEP and IPCC assessments. In particular, the WMO/UNEP assessment brings together several hundred scientists from around the world to review data, prepare the chapters, and provide peer review for the report. NASA personnel and grantees have been intimately involved in all stages of this effort for well over a decade, and work with others to prepare detailed summaries of issues of atmospheric relevance as needed to support the assessment process.

As more nations of the world introduce space-based measuring programs, NASA's participation in international cooperative activities will only increase. For example, space-based instruments which measure atmospheric ozone (and in many cases, related trace constituents) are planned for launch by several foreign partners over the next few years. A summary of past, present, and future space-based ozone-measuring instruments is given in Figure 6. These include the European Space Agency's (ESA's) Global Ozone Monitoring Experiment (GOME) launched aboard the ERS-2 satellite this past April, the ISTOK-1 and OZON-MIR instruments launched on the PRIRODA

module for the Russian MIR space station in spring 1996, the German/Russian MIRIAM/DOPI instruments scheduled to be launched to PRIRODA in the fall of 1996, the IMG, ILAS, and RIS instruments to be flown on the Japanese ADEOS spacecraft in summer 1996, and the SCIAMACHY, GOMOS, and MIPAS instruments to be launched aboard the European ENVISAT in 1999, and the Chilean-built OLME instrument, planned for launch on their FaSAT Bravo satellite (the launch of the FaSAT Alpha satellite, which contained the first version of this instrument was a failure).

In the long-term, cooperation of NASA, NOAA, our foreign partners, and the international science community are all needed if an effective space-based ozone monitoring strategy is to be put together. The highest priority is that a continuous set (covering both total ozone and vertical profile, including some direct measurement of tropospheric ozone) of high quality measurements be made. The partitioning of that effort among the possible contributors, both through operational programs (US NPOESS, EUMETSAT METOP) and research programs (e.g., US EOS, Japanese ADEOS and its successors), needs to be worked out. Coordination and utilization of the whole array of available balloon-, aircraft-, and ground-based sensors, along with supporting research and modeling/ analysis activities, are also needed to most efficiently advance our scientific understanding of the atmosphere.

C. Peer-Led Science Planning Groups

The two peer-led scientific planning groups most relevant to NASA's ozone and atmospheric chemistry research are the World Climate Research Program, through its Stratospheric Processes and their Role in Climate (SPARC) subgroup, and the International Geosphere-Biosphere Program (IGBP) through its International Global Atmospheric Chemistry (IGAC) program.

Plans are underway through a subgroup being set up under SPARC, together with the World Meteorological Organization and the International Ozone Commission, to try to coordinate future space-based ozone measurements. Calibration and validation plans need to be established. It is likely that the NDSC will provide a critical role in the on-orbit validation of all these spacecraft. NASA has the potential to play a fundamental role in the development of calibration plans for ozone instruments, especially in the ultraviolet.

Under the IGAC program, there are several activities, including the Global Emissions Inventory Activity (GEIA), Global Observations of Atmospheric Chemistry (GLOCHEM), and Global Integration and Modeling (GIM). The recent merger of the International Global Aerosol Program (IGAP) into IGAC has led to the formation of IGAC-FAA (Focus on Atmospheric Aerosols) which will also provide a good coordinating mechanism for NASA's chemistry-related aerosol research.

VI. FUTURE EMPHASES AND CONNECTIONS

NASA's ozone program will likely change in an "evolutionary" way over the next decade. The continued thrust will be to reduce uncertainties in our knowledge of atmospheric processes, our quantitative understanding of long-term atmospheric changes, and our ability to forecast the future chemical state of the atmosphere using computational models. While in the past NASA's program in atmospheric chemistry was very strongly stratospherically-dominated, the efforts in stratospheric and tropospheric research are expected to become more equivalent in the coming decade.

These plans are indicated schematically in Figure 7 which shows a 10-year plan for NASA's ozone program, broken up according to the six approaches of the previous section. Of course, one cannot be too complacent in foreseeing the future—a 10-year plan produced just over a decade ago might have completely ignored the issue of polar ozone depletion, which was not discovered until 1985!

There are three areas where progress may be more than incremental, however. These arise from the projected availability of launches of newly-developed satellite instruments, new aircraft which provide opportunities for *in situ* and remotely-sensed measurements, and high performance computing equipment which will facilitate the construction and use of improved three-dimensional troposphere/stratospheric chemistry/transport models. Brief summaries of the impacts of these capabilities follow.

The launch of spacecraft in the EOS program, as noted in Section III.E, will have a major impact on NASA's atmospheric chemistry program. Key datasets to come from these will include global measurements of vertically-resolved tropospheric carbon monoxide (as well as column integrated methane) from the Measurement of Pollution in the Troposphere (MOPITT) instrument on the first EOS spacecraft (EOS-AM) in 1998, measurements of stratospheric and upper tropospheric aerosols, ozone, and other trace constituents from SAGE III (launches in 1998 and 2001), and global measurements of most important trace constituents in the troposphere and stratosphere aboard EOS CHEM in 2002. Included in these will be the first-ever global measurements of vertically-resolved tropospheric ozone and its precursors from the TES instrument, extended global measurement of small-scale structure in stratospheric trace constituent distributions from the HIRDLS instrument, and extended global measurements of lower stratospheric OH from the MLS instrument.

New aircraft platforms, especially uncrewed aerial vehicles (UAVs, see Section III.D) will potentially provide opportunities for measurements at higher altitudes and with very different operational characteristics (e.g., longer flights) than with currently available platforms. Instruments for these aircraft are currently under development through the ERAST program (see Section IV.B.1).

Finally, improvements in high performance computing (both hardware and computational and numerical algorithms) have the potential to allow for the use of three-dimensional coupled chemistry/transport models for the troposphere and stratosphere which would be impractical with

current computing capability. Development of algorithms and combined modules for this work is currently supported through NASA's HPCC program. It is expected that the routine use of the core model being developed under AEAP (with ACMAP support and participation) hinges on the availability of this improved computing power.

There are also several new opportunities and initiatives which will be pursued under NASA's ozone and atmospheric chemistry program which represent changes in emphasis and/or direction from previously, however. These are summarized as follows:

A. Chemistry-Climate Coupling

NASA's ozone and climate research will be increasingly interactive. In the upper troposphere, ozone is a strong climate gas, but one whose distribution is controlled through a complicated set of chemical reactions (and which are closely tied to transport processes such as convection and stratosphere/troposphere exchange). In the lower stratosphere ozone depletion can also lead to reduced ultraviolet heating, and models must therefore simulate the chemistry (and aerosol behavior) there. Further, cooling of the global stratosphere expected due to increased carbon dioxide and reduced ozone can affect ozone destruction, especially through changes in reaction rates and changed formation of polar stratospheric clouds and aerosols. Such couplings are highly non-linear, and have the potential to lead to major effects if "threshold" behaviors are reached.

Other research has shown that tropospheric aerosols, especially those in the lower troposphere which form from oxidation of anthropogenically-generated sulfur compounds, may be important for climate. The formation of these aerosols is essentially chemically-driven, beginning with the oxidation of sulfur dioxide by hydroxyl, for instance. In the longer-term ozone-oriented chemistry-climate models and radiatively-oriented models of atmospheric aerosols will likely become unified into more general "chemistry-climate" models. These will place enormous demands on computing capability, and progress in this area will likely rely on use of highly parallel computing equipment and specifically-designed algorithms. This is an issue for which close collaboration with NASA's High Performance Computing (HPCC) program is greatly desired.

An example of the implementation of this tie is NASA's recent selection of several tasks in this area as part of an augmentation of IDS activities of the EOS. Three major modeling efforts were selected, as well as several more process-oriented tasks which should facilitate the development of future coupled models.

Finally, there has recently been a recognition that the stratosphere can exert a significant downward forcing on the troposphere. A particularly interesting component of this forcing is that due to the large solar cycle associated with the absorption of short-wavelength ultraviolet radiation by stratospheric ozone, and the resulting small changes in circulation. Coupled troposphere-stratosphere transport models which include realistic representations of the dynamical feedbacks between stratospheric ozone, stratospheric circulation, and tropospheric circulation, will be needed for the downward control to be simulated.

B. Constituent Assimilation

Data assimilation has been a widely-used tool in the meteorological community. In data assimilation, observations and models are combined in a way to produce geophysically consistent and accurate global fields of temperatures, winds, and other parameters. The use of data assimilation has evolved far beyond its initial one to provide balanced initial conditions for numerical weather prediction. It now occupies a central role in atmospheric science in providing accurate daily global fields of numerous parameters.

In the future, data assimilation is likely to include trace constituents in addition to the meteorological parameters. Initial experiments assimilating nitrous oxide observations from UARS are showing the utility of the data assimilation process. In the short term, assimilation of ozone will be used to help improve short-term forecasts of ozone variability to improve UV exposure indices (this is collaborative work with NOAA). In the longer term, there are plans to assimilate several atmospheric trace species. This will be done in conjunction with the EOS program, which will provide global data on numerous trace constituents in the troposphere and stratosphere. The most straightforward application of constituent assimilation is to long-lived tracers, but application to ozone and ultimately intermediate-lived tropospheric compounds (such as carbon monoxide), is also planned.

C. Atmospheric Chemistry-Aerosol Interface

In the past, there has been little overlap between NASA's research on tropospheric aerosols, which have emphasized their radiative effects, and tropospheric chemistry, which has emphasized the oxidizing capacity of the free troposphere. In the foreseeable future, we see much more attention paid to the chemical processes which are responsible for formation of atmospheric aerosols, those which may occur on the surface of aerosols, and the connection between aerosol composition and radiative properties. This will likely involve a combination of laboratory and field experiments, as well as the inclusion of tropospheric aerosol distributions and properties into tropospheric chemistry/transport models (see Section IV.B.1 above). As an example, both atmospheric chemistry and radiation measurements are expected to be part of the planned Aerosol Characterization Experiments (ACE) and the Tropospheric Aerosol Radiative Forcing Experiment (TARFOX).

There will also be increasing attention paid to maximizing the information on tropospheric aerosols which can be obtained from datasets which were originally developed for chemical purposes. For example, a good measure of tropospheric aerosol burden is now inferred from TOMS measurements, using a technique based on differences between albedo in two long wavelength reflectivity channels. This product needs to be carefully validated by comparison with surface measurements of optical depth. Measurements of aerosol profiles in the upper troposphere have been made using SAGE following development of an algorithm to separate aerosol-created opacity from that arising from clouds. Additional validation of this algorithm is needed.

Finally, there is a need for instruments which can make *in situ* aircraft measurements of the chemical composition of atmospheric aerosols. Work has begun on instruments to do this, and completion of these instruments remains a high priority of NASA's overall efforts in this area.

D. Atmosphere-Land and Atmosphere-Ocean Interface

Models provide an important integrative tool for using global measurements of atmospheric trace constituent composition and measurements of surface biogeochemical processes. Models may be especially useful in providing tests of the consistency of known information about surface production and destruction of trace gases, atmospheric destruction, and atmospheric transport. This approach has been used in the past with good success in studying the distribution of CFCs and related molecules in the troposphere. This can include species produced both at the land surface, notably methane, as well as those produced and/or destroyed in the ocean, such as methyl bromide. A particular near-term focus may be on whether or not one can use a combined global atmospheric chemistry/transport model with a land biogeochemistry model to understand the interannual variability in the growth rate of atmospheric methane. Later on, similar models which improved representation of the atmosphere/ocean interface, as well as of biological and chemical processes which result in the production and destruction of methyl bromide may be used to help simulate that compound's behavior.

E. Air Quality

NASA's research on tropospheric ozone has focused on the global atmosphere, with an emphasis on remote areas of the troposphere. This has helped differentiate NASA's research from that of EPA and DOE, which typically focused on polluted areas, especially those in the US. There has been increasing attention in the past few years on how developed areas influence ozone distributions in remote areas, and such efforts are expected to continue, especially as the importance of understanding background ozone concentration increases. In particular, the possibility exists that significant changes in background ozone concentration will have an effect on local/regional air quality with possible repercussions for achieving levels of mandated standards.

NASA's expertise in modeling, remote sensing, laboratory measurements of rates of fundamental processes, and in aircraft-based *in situ* and remote measurements will come to bear on this problem. NASA will also be prepared to make unique contributions to the North American Research Strategy for Tropospheric Ozone (NARSTO) effort recently initiated by the Air Quality Research Subcommittee of the Committee on the Environment and Natural Resources. One potential area for specific NASA contribution to NARSTO is evaluation of the role which downward transport of stratospheric or upper tropospheric ozone has on local/regional ozone budgets; discussions have begun on the possibility of NASA organizing or co-organizing a workshop on this subject for NARSTO.

Methods to infer tropospheric ozone from space-based measurements, either directly from TOMS data or from the residual between TOMS and SBUV/2 or TOMS and SAGE data, have been carried out with some success. The TES instrument will provide significant information on tropospheric ozone and other constituents in the post-2002 time frame. Additional research to further develop these techniques and to help define under what conditions they are expected to have use, will continue over the next few years. It is possible that simple instruments which can directly measure tropospheric ozone will be developed under the NMP and/or ESSP programs.

Finally, it is important to note the natural tie between regional and global atmospheric models, especially in areas of surface sources and deposition of trace species. Both global and regional models need spatially and temporally resolved fluxes of trace constituents. Similarly, removal of soluble species, especially sulfur and nitrogen oxides, from global models will be carried out by the same processes that lead to acid deposition. Modules for these processes may be common to both the air quality and global change communities, and databases must be accessible to both. To help support efforts in this area, especially on surface sources, NASA plans to participate in the Global Emissions Inventory Activity (GEIA) of the IGBP IGAC project, under which spatially and temporally resolved emission inventories for oxides of nitrogen and sulfur, as well as organic compounds, are being developed.

F. Applications

NASA scientists have recently shown that a relatively simple model of ultraviolet radiative transfer, including cloud effects, can provide a good representation of surface ultraviolet flux given total ozone measurements. Plans are to make daily maps of inferred surface ultraviolet radiation available on a regular basis following the launch of Earth Probe and ADEOS TOMS, and retrospective studies to produce information about past surface UV flux are underway. The stratospheric ozone-UV flux relationship may be used together with the stratospheric ozone data to support the "UV-forecasting" network of NOAA and EPA.

The Federal Aviation Administration (FAA) and NASA have signed a memorandum of understanding to consider the use of TOMS ozone data by the FAA to help plan more efficient routing of jet aircraft. Although the theoretical basis for these efforts is not well established, there is anecdotal evidence suggesting that TOMS data can help "find the jet stream" in near-real time, and that more efficient aircraft routes can be developed using TOMS data. The FAA also wants to use information on sulfur dioxide from TOMS to help pinpoint regions of volcanic cloud hazards in aviation, so that aircraft may be routed around these regions. NASA is supporting the development of improved SO_2-algorithms for TOMS, and these will be provided to the FAA.

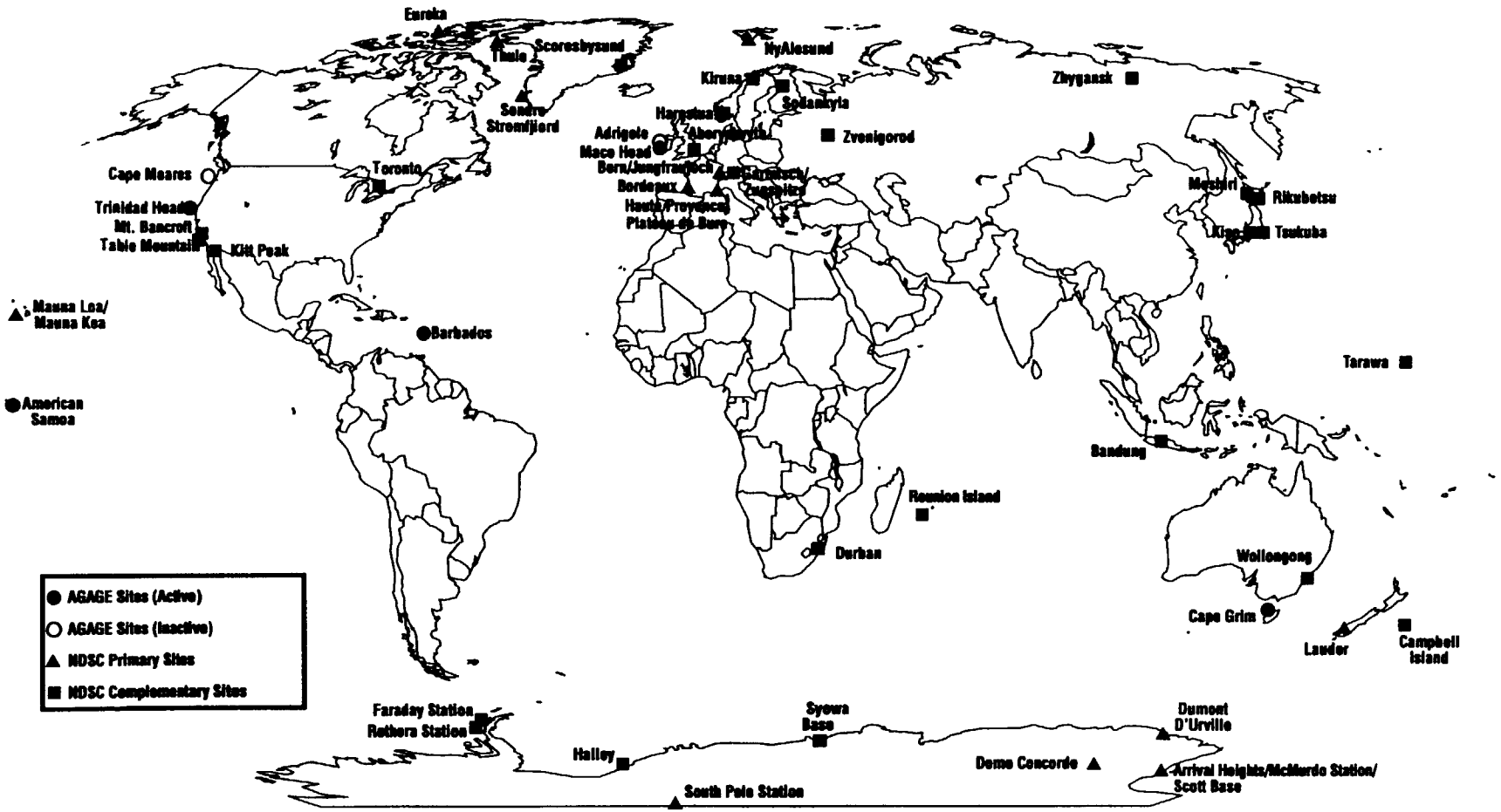

Figure 1. Map showing geographic locations of AGAGE ground measurement sites and NDSC primary and complementary sites. Note that Trinidad Head AGAGE station does not begin operating until 1996, while period of operation for Irish stations was 1978-1983 for Adrigole and since 1987 for Mace Head. The Cape Meares station operated only from 1980 to 1989.

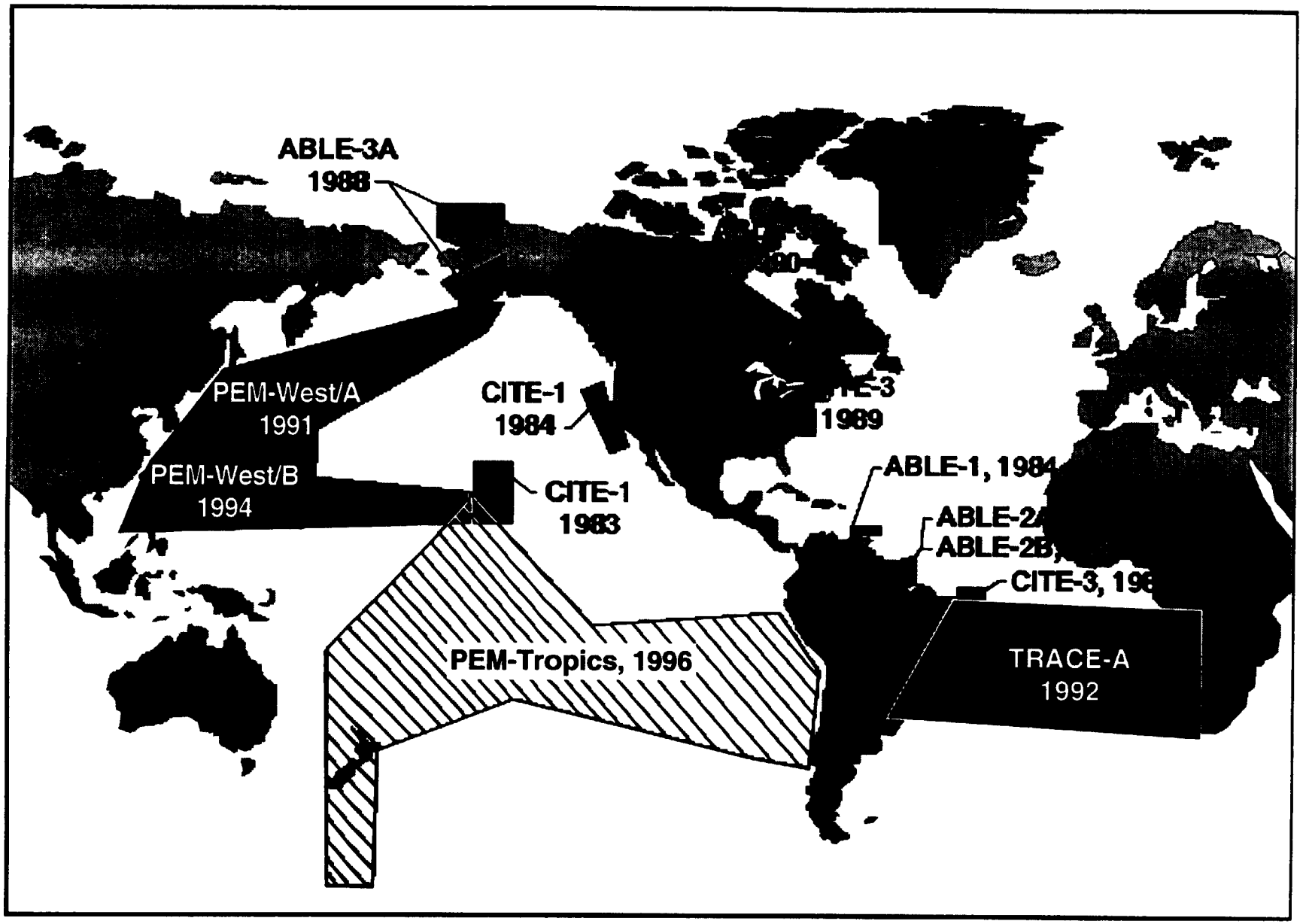

Figure 2. Map showing geographic distribution, chronology, and names of Global Tropospheric Experiment (GTE) aircraft missions carried out as part of NASA's tropospheric ozone research activities.

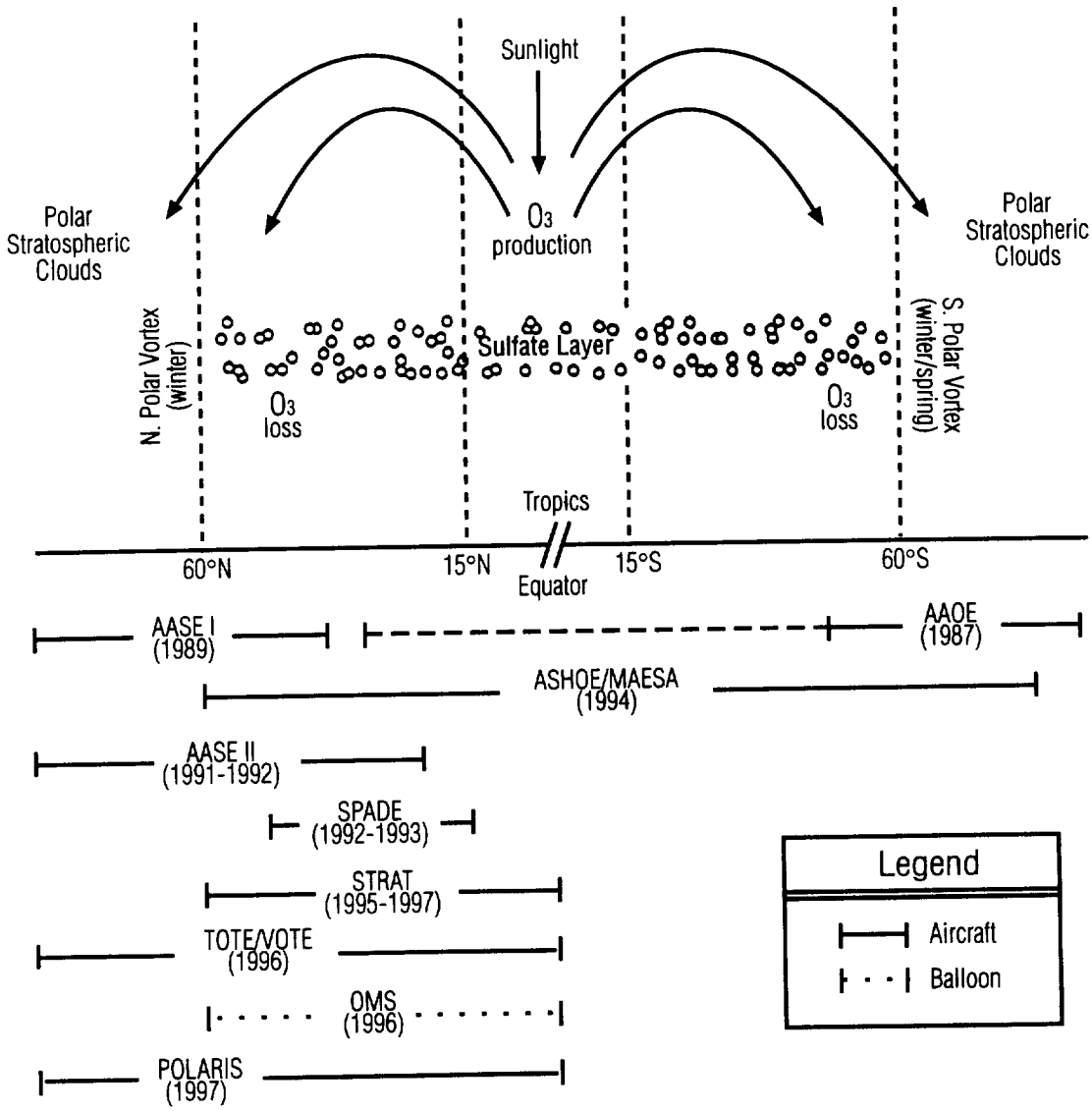

Figure 3. Schematic diagram showing latitudinal distribution and chronology of stratospheric aircraft missions along with representation of significant processes affecting stratospheric ozone distributions.

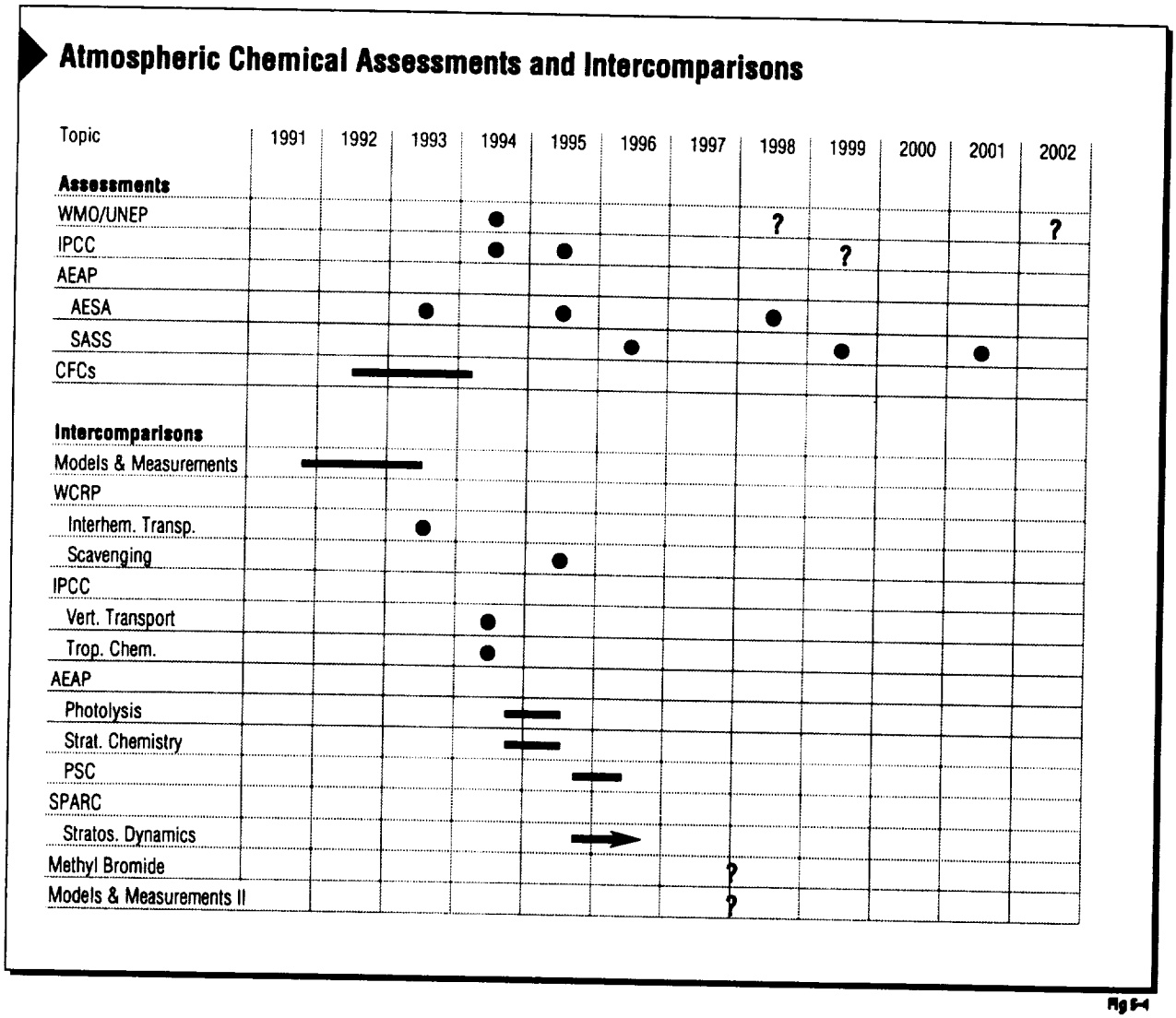

Figure 4. Timeline showing assessments and intercomparisons for atmospheric chemistry.

Schematic Heirarchy of Atmospheric Chemistry Models

Class of Model	
0-D	Photochemical Box Model
1-D	Steady-state: some constituents prescribed from measurements Time evolving
2-D	Choices of dynamics: Fixed K_{yy}, etc. / K_{yy} from data / Interactive Dynamics / wave-breaking parameterizations Evolution of chemistry: Gas phase only; chemistry now includes reactions on aerosols, PSCs
Parcel Trajectory	Basic trajectory / Contour advection / Reverse domain filling
3-D	Low resolution 3-D models (e.g., 3 wave models) *Off-line models* (stratosphere typically before troposphere) - Choice of winds: - mechanistic models - GCMs - strat. analysis (forced at bottom) - data assimilation *On-line models* - interactive radiation/dynamics (prescribed chem., e.g., O_3 hole) - fully interactive models

Figure 5. *Schematic diagram showing hierarchy of atmospheric chemistry models, broken down by class (box, parcel trajectory, 1-D, 2-D, 3-D) showing options for different aspects of models.*

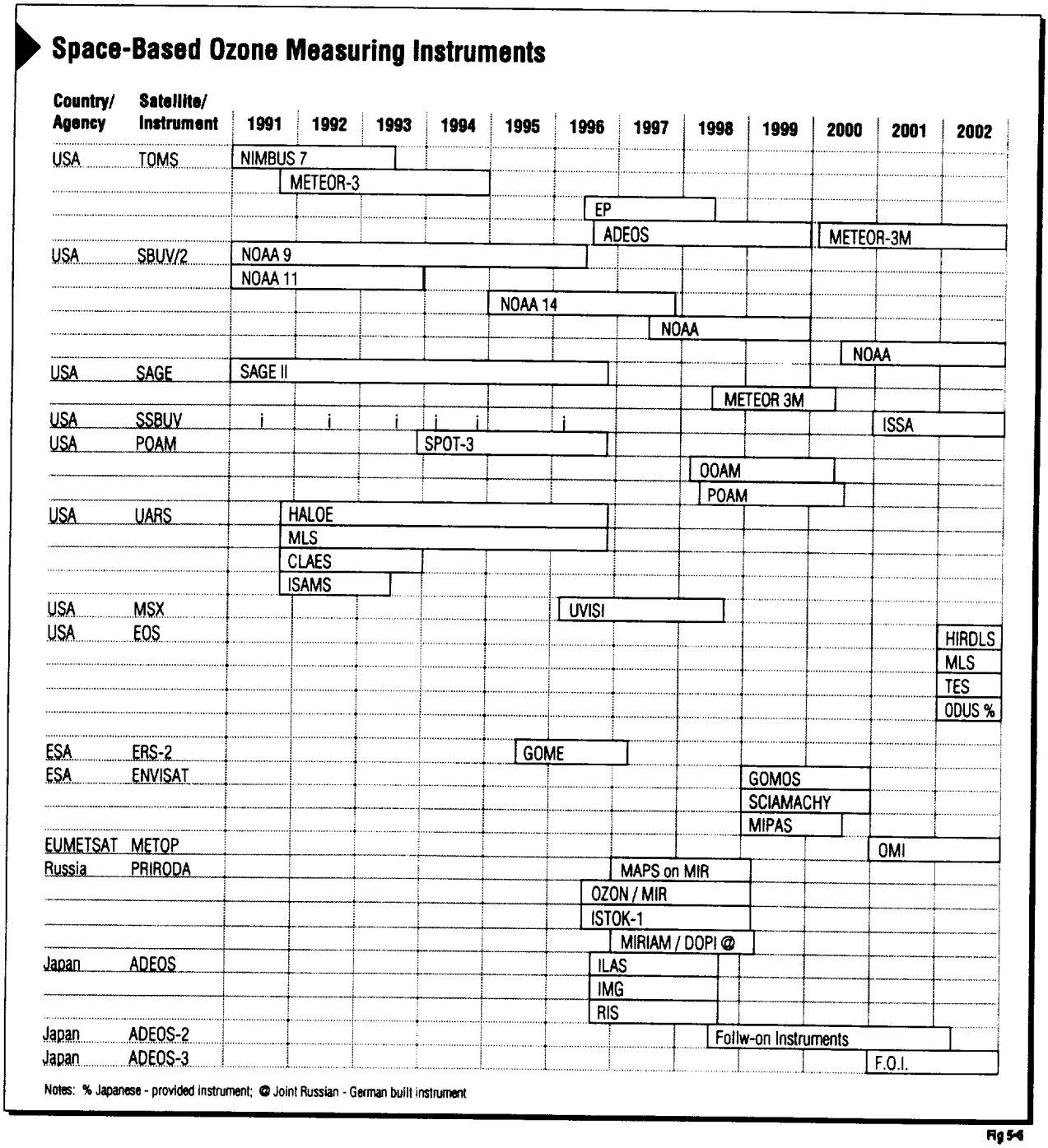

Figure 6. Timeline showing past, present, and projected future space-based ozone measurements organized by launching nation/agency, showing platforms and instruments. Potential instruments, or known instruments with launch information unknown are shown at the bottom. Dates are approximate.

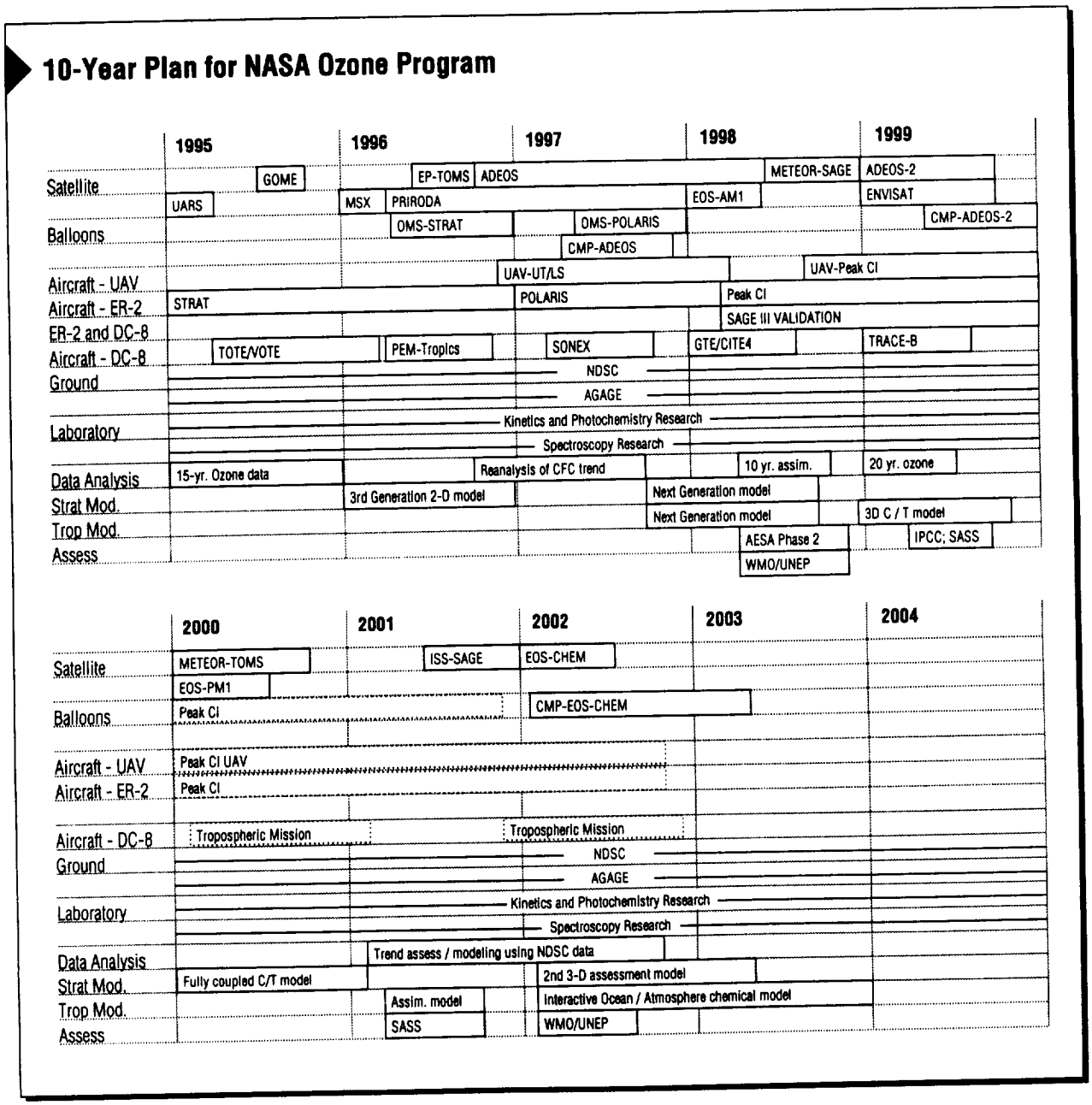

Figure 7. 10-year plan for NASA ozone program, with different program elements organized according to six techniques in Section III of this report.

TABLE 1. Constituents

	AGAGE	NDSC	DC-8	ER-2	Balloon	Shuttle	Satellite*	Planned† Satellite
P,T		P	P	I	I	P	P	P
Aerosols		P	P	I, P	I		P	P
Winds				I	I			
O_3		P, C	I, P, C	I	I, P	P, C	P, C	P, C
H_2O		P, C	I, P, C	I,P,C	I, P	P	P	P
CO_2	(I)		I	I	I, P	P		
N_2O	I	P, C	I, P	I	I, P	P	P	P
CH_4	I	C	I, P, C	I	I, P	P	P	P, C
CO	I	P, C	I	I	P	P		P, C
CFC-11	I	C	I	I	P	P		P
CFC-12	I	C	I	I	P	P		P
CFC-113	I		I	I	P			
HCFC-22	I	C	I, P	I	P	P		
HCFC-123	I		I	I				
HCFC-142b	I		I	I				
HCFC-141b	I		I	I				
CH_3Cl	I		I	I		P		
CCl_4	I		I	I	P	P		
$CHCl_3$	I		I	I				
CH_2Cl_2			I	I				
CH_3CCl_3	I		I	I				
COF_2		C	P		P	P		
CF_4	I		C		P	P		
C_2H_6		C	I	I		P		
CH_3Br	I		I	I				
SF_6	I	C		I	(I)	P		
NO		C	I	I	I, P	P	P	P
NO_2		C	I	I	I, P	P	P	P, C
NO_3								P
HNO_3		C	I, P		I, P	P		P
$ClNO_3$		C	C	(I)	P	P		P
N_2O_5			I		P	P		P
HNO_4			I			P		
PAN			I					
NO_y			I	I	I	P		
HCl		C	P, C	I	P	P	P	P
HF		C	P, C		P	P	P	
HBr								

KEY
I-*In situ*
P-Profile
C-Column
( )-Planned

* Currently operating, NASA-supported instruments/satellites

† NASA-supported instruments/satellites

TABLE 1. (Continued)

	AGAGE	NDSC	DC-8	ER-2	Balloon	Shuttle	Satellite*	Planned† Satellite	
OH		C	P, C	I	I, P			P	KEY
HO_2			P, C	I	I, P				I-*In situ*
H_2O_2			P, C		P				P-Profile
HDO			P, C		P		P		C-Column
ClO		P, C		I	I, P		P	P	()-Planned
OClO		C						P	
BrO		C		I	I				
HOCl			C		P				
HCN		C	P, C		P	P			
SO_2			I			P	C	C	
DMS			I						
OCS		C	I, P, C		P		P		
UV_B Flux		C							
UV Flux			I	I					
Halon-1211			I	I					
H_2				I	P				
O_2			C		P, C				
N_2			C		P, C				

* Currently operating, NASA-supported instruments/satellites

† NASA-supported instruments/satellites

ACRONYMS AND ABBREVIATIONS

AAOE	Airborne Antarctic Ozone Experiment
AASE	Airborne Arctic Stratospheric Expedition
ACE	Aerosol Characterization Experiment
ACMAP	Atmospheric Chemistry and Modeling Analysis Program
ADEOS	Advanced Earth Observing System
AEAP	Atmospheric Effects of Aviation Project
AESA	Atmospheric Effects of Stratospheric Aircraft Program
AGAGE	Advanced Global Atmospheric Gas Experiment
ALE	Atmospheric Lifetime Experiment
ASHOE	Airborne Southern Hemisphere Ozone Experiment
ATLAS	Atmospheric Laboratory for Applications and Science
ATMOS	Atmospheric Trace Molecule Spectroscopy
CFC	Chlorofluorocarbon
CHEM	Chemistry Mission
CRISTA/SPAS	Cryogenic Infrared Spectrometer and Telescopes for the Atmosphere/Shuttle Pallet Satellite
DOD	Department of Defense
DOE	Department of Energy
ENVISAT	Environmental Satellite
ERS-2	Environmental Remote Sensing Satellite-2
EOS	Earth Observing System
EPA	Environmental Protection Agency
ERAST	Environmental Research Aircraft and Sensor Technology Program
ESSP	Earth System Science Pathfinders
FAA	Federal Aviation Administration
FSD	Flight Systems Division
GEIA	Global Emissions Inventory Activity
GIM	Global Intergration and Modeling
GIP	Guest Investigator Program
GLOCHEM	Global Observations of Atmospheric Chemistry
GOME	Global Ozone Mapping Experiment
GOMOS	Global Ozone Monitoring by Occultation of Stars
GSFC	Goddard Space Flight Center
GTE	Global Tropospheric Experiment
HCFC	Hydrochlorofluorocarbons
HIRDLS	High-Resolution Dynamics Limb Sounder
HPCC	High Performance Computing and Communications
HSRP	High Speed Research Program
IDS	Interdisciplinary Science Program
IGAC	International Global Atmospheric Chemistry
IGAP	International Global Aerosol Program
IGBP	International Geosphere-Biosphere Program
ILAS	Improved Limb Atmospheric Spectrometer
IMG	Interferometric Monitor for Greenhouse Gases

IPCC	Intergovernmental Panel on Climate Change
ISTOK-1	Infrared Spectroradiometer on Mir
LIMS	Limb Infrared Monitor of the Stratosphere
MAESA	Measurements for Assessing the Effects of Stratospheric Aircraft
MAHRSI	Middle Atmosphere High Resolution Spectrograph Investigation
MAPS	Measurement of Air Pollution from Satellites
METOP	Meteorological Operational Weather Satellite
MIPAS	Michelson Interferometer for Passive Atmospheric Sounding
MIRAS	Mir Infrared Atmospheric Sounder
MIRIAM/DOPI	Mir Infrared Atmospheric Measurements/Double Pendulum Interferometer
MLS	Microwave Limb Sounder
MO&DA	Mission Operations and Data Analysis
MOPITT	Measurement of Pollution in the Troposphere
MSX	Midcourse Space Experiment
NARSTO	North American Research Strategy for Troposheric Ozone
NASA	National Aeronautics and Space Administration
NCEP	National Meteorological Center for Environmental Protection
NDSC	Network for the Detection of Stratospheric Change
NESDIS	National Environmental Satellite and Information Service
NIST	National Institute of Standards and Technology
NMP	New Millenium Program
NOAA	National Oceanic and Atmospheric Administration
NPOESS	National Polar Orbiting Environmental Satellite System
NRA	NASA Research Announcement
NSF	National Science Foundation
ODIS	Operations Data and Information Systems
ODUS	Ozone Dynamics Ultraviolet Spectrometer
OLME	Ozone Layer Monitoring Experiment
OMTPE	Office of Mission to Planet Earth
OOAM	Orbit Ozone Aerosol Monitor
PEM	Pacific Exploratory Mission
POAM	Polar Ozone and Aerosols Mission
POLARIS	Photochemistry of Ozone Loss in the Arctic Region in Summer
OZON-MIR	Ozone Trace Gas and Aerosol Monitor on Mir
RIS	Retroreflector in Space
RPA	Remotely Piloted Aircraft
SAGE	Stratospheric Aerosol and Gas Experiment
SASS	Subsonic Assessment
SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Cartography
SBUV/2	Solar Backscatter Ultraviolet spectrometer/2
SOLSE	Shuttle Ozone Limb Sounder Experiment
SONEX	Subsonic Ozone and Nitrogen Experiment
SPADE	Stratospheric Photochemistry, Aerosols and Dynamics Expedition
SPARC	Stratospheric Processes And their Role in Climate
SSBUV	Shuttle Solar Backscatter Ultraviolet spectrometer
STRAT	Stratospheric Tracers of Atmospheric Transport

TARFOX	Tropospheric Aerosol Radiative Forcing Experiment
TCP	Tropospheric Chemistry Program
TES	Tropospheric Emission Spectrometer
TOMS	Total Ozone Mapping Spectrometer
TOTE	Tropical Ozone Transport Experiment
TRACE	Transport and Atmospheric Chemistry Experiment
UARP	Upper Atmospheric Research Program
UARS	Upper Atmospheric Research Satellite
UNEP	United Nations Environment Program
UV	Ultraviolet
UVISI	Ultraviolet and Visible Imagers and Spectrographic Imagers
VOTE	Vortex Ozone Transport Experiment
WCRP	World Climatic Research Program
WMO	World Meteorological Organization

WEB SITES FOR ATMOSPHERIC OZONE

ADEOS
http://hdsn.eoc.nasda.go.jp/guide/guide/satellite/satdata/adeos_e.html

AGAGE
http://cdiac.esd.ornl.gov/cdiac/ndps/db1001.html

ATLAS
http://wwwghcc.msfc.nasa.gov/atlas.html

ATMOS
http://remus.jpl.nasa.gov/

DAACs
http://eosdis.larc.nasa.gov/handbook/daac_glossary.html

DC-8
http://airsci-www.arc.nasa.gov/DC-8/dc8page.html

EOS
http://spso.gsfc.nasa.gov/spso_homepage.html

EOSDIS
http://spsosun.gsfc.nasa.gov/ESDIShome.html

EOS/IDS
http://spso.gsfc.nasa.gov/directory/ids/ids.html

ENVISAT
http://gds.esrin.esa.it/Ce3.1.3;sk=F1A64C9E

ER-2
http://airsci-www.arc.nasa.gov/ER-2/AIRPROGL.HTM

ESA
http://gds.esrin.esa.it:80/home;sk=F1A64C9E

GEIA
http://neonet.nlr.nl/ceos/GEIA.html

GOME
http://www.jw.estec.esa.nl:8080/gome.index.html

IGAC
http://web.mit.edu/igac/www/

LITE
http://arbs8.larc.nasa.gov/LITE/litehome.html

MAPS
http://stormy.larc.nasa.gov/overview.html

MSX
http://msx.nrl.navy.mil/

OMTPE
http://www.hq.nasa.gov/office/mtpe/

NASA
http://www.nasa.gov/

NATIONAL CENTER FOR ATMOSPHERIC RESEARCH (NCAR)
http://www.ucar.edu/org/ncar/index.html

NDSC
http://climon.wwb.noaa.gov/

PRIRODA
http://www.ire.rssi.ru/priroda/priroda.htm

RUSSIAN ACADEMY OF SCIENCES
http://www.RAS.ru/RAS/index.html

SAGE
http://asd-www.larc.nasa.gov/sage/ASDsage.html

SATELLITE WEATHER INFORMATION FOR STRATOSPHERIC SCIENCES (SWISS)
http://telsci.arc.nasa.gov/pages/tote1.html

SPACE RESEARCH INSTITUTE/RUSSIAN ACADEMY OF SCIENCES
http://www.iki.rssi.ru/Welcome.html

SPARC
http://www.sparc.com/

SSBUV
http://ssbuv.gsfc.nasa.gov/

STRAT
http://hyperion.gsfc.nasa.gov/Aircraft/strat/strat.html

TARFOX
http://prometheus.arc.nasa.gov/~tarfox/

THESEUS
http://www.hq.nasa.gov/office/mtpe/Theseus.html

TOMS
http://jwocky.gsfc.nasa.gov/

TOTE/VOTE
http://hyperion.gsfc.nasa.gov/Aircraft/tote/vote_top.html

UARS
http://daac.gsfc.nasa.gov/CAMPAIGN_DOCS/UARS_project.html

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	February, 1997	Final. (1 Oct. 1993 - 30 Sept. 1996)

4. TITLE AND SUBTITLE
Present State of Knowledge of the Upper Atmosphere 1996: An Assessment Report: Report to Congress and the Environmental Protection Agency.

5. FUNDING NUMBERS

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
NASA Office of Mission to Planet Earth Science Division

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Aeronautics and Space Administration
Washington, DC 20546

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unclassified, Unlimited
Subject Category 46

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)* This document is issued in response to the Clean Air Act Amendment of 1990, Public Law 101-549, which mandates that the National Aeronautics and Space Administration (NASA) and other key agencies submit triennial report to congress and the Environmental Protection Agency. NASA is charged with the responsibility to report on the state of our knowledge of the Earth's upper atmosphere, particular the Stratosphere. Part I of this report summarizes the objectives, status, and accomplishments of the research tasks supported under NASA's Upper Atmosphere Research Program and Atmospheric Chemistry Modeling and Analysis Program for the period of 1994-1996. Part II (this document) presents summaries of several scientific assessments, reviews, and summaries. These include the executive summaries of two scientific assessments: (Section B) "Scientific Assessment of Ozone Depletion: 1994"; (Section C) "1995 Scientific Assessment of the Atmospheric Effects of Stratospheric Aircraft); end of mission/series statements for three stratospherically-focused measurment campaigns: (Section D) "ATLAS End-of-Series Statement"; (Section E) "ASHOE/MAESA End-of-Mission Statement"; (Section F) "TOTE/VOTE End-of-Mission Statement"; a summary of NASA's latest biennial review of fundamental photochemical processes important to atmospheric chemistry "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling"; and (Section H) the section "Atmospheric Ozone Research" from the Mission to Planet Earth Science Research Plan, which describes NASA's current and future reasearch activities related to both tropospheric and stratospheric chemistry.(cont.)

14. SUBJECT TERMS	15. NUMBER OF PAGES
Ozone, Polar Ozone, Chlorofluorocarbons, CFC's, model results, stratosphere, assessment, PSCs, Montreal Protocol, chemical kinetics, photo chemistry, methyl bromide, supersonic aircraft	180
	16. PRICE CODE: Aut

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std 239-18
298-102

A list of contributors to each of the included documents is included with this report.

NASA's Upper Atmosphere Research Program (UARP) and Atmospheric Chemistry Modeling and Analysis Program (ACMAP)

February 1997

RESEARCH SUMMARIES

1994 – 1996

Report to Congress and the Environmental Protection Agency

National Aeronautics and Space Administration
Washington, DC 20546

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PREFACE

NASA has relied heavily on the entire scientific community, national and international, in its effort to provide a better understanding of the upper atmosphere and its perturbation in response to natural phenomena and human activities. The lists of contributors to the individual sections in this report are given in Section I. We are indebted to those who gave their time and knowledge. Specifically, we would like to thank the investigators and collaborators for providing information on their specific tasks. We also thank Rose Kendall and Kathy Wolfe for compiling the report and providing editorial support.

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INTRODUCTION

INTRODUCTION

Under the mandate contained in the FY 1976 NASA Authorization Act, the National Aeronautics and Space Administration (NASA) has developed and is implementing a comprehensive program of research, technology, and monitoring of the Earth's upper atmosphere, with emphasis on the stratosphere. This program aims at expanding our understanding to permit both the quantitative analysis of current perturbations as well as the assessment of possible future changes in this important region of our environment. It is carried out jointly by the Upper Atmosphere Research Program (UARP) and the Atmospheric Chemistry Modeling and Analysis Program (ACMAP), both managed within the Science Division in the Office of Mission to Planet Earth at NASA. Significant contributions to this effort are also provided by the Atmospheric Effects of Aviation Project (AEAP) of NASA's Office of Aeronautics. The long-term objectives of the present program are to perform research to:

- understand the physics, chemistry, and transport processes of the upper atmosphere and their effect on the distribution of chemical species in the stratosphere, such as ozone;
- understand the relationship of the trace constituent composition of the lower stratosphere and the lower troposphere to the radiative balance and temperature distribution of the Earth's atmosphere; and
- accurately assess possible perturbations of the upper atmosphere caused by human activities as well as by natural phenomena.

In compliance with the Clean Air Act Amendments of 1990, Public Law 101-549, NASA has prepared a report on the state of our knowledge of the Earth's upper atmosphere, particularly the stratosphere, and on the progress of UARP and ACMAP. The report for the year 1996 is composed of two parts. Part I summarizes the objectives, status, and accomplishments of the research tasks supported under NASA UARP and ACMAP in a document entitled, *Research Summaries 1994-1996.* Part II is entitled *Present State of Knowledge of the Upper Atmosphere 1996: An Assessment Report.* It consists primarily of the Executive Summary and Chapter Summaries of the World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 37, *Scientific Assessment of Ozone Depletion: 1994*, sponsored by NASA, the National Oceanic and Atmospheric Administration (NOAA), the UK Department of the Environment, the United Nations Environment Program, and the World Meteorological Organization. Other sections of Part II include summaries of the following: an Atmospheric Ozone Research Plan from NASA's Office of Mission to Planet Earth; summaries from a series of Space Shuttle-based missions and two recent airborne measurement campaigns; the Executive Summary of the 1995 Scientific Assessment of the Atmospheric Effects of Stratospheric Aircraft, and the most recent evaluation of photochemical and chemical kinetics data (Evaluation No. 12 of the NASA Panel for Data Evaluation) used as input parameters for atmospheric models.

This NASA program supports a variety of research tasks proposed by scientists from the university, government, and industrial research communities. It also sponsors periodic assessments of the state of our knowledge of the stratosphere and its response to specific perturbations such as releases of halocarbons, aircraft effluents, and other potential pollutants, as well as due to natural forcings such as volcanic eruptions. Funding of the research program was approximately $24M in FY 1996. Substantial advances in our knowledge of the upper atmosphere have been made in each of the major fields of research outlined below.

UARP activities fall into three broad categories: (1) field measurements (employing *in situ* and remote sensing techniques from ground-based, aircraft, balloon, and rocket platforms); (2) laboratory studies (gas-phase and heterogeneous kinetics, photochemistry, spectroscopy, and calibration standards development); and (3) process study modeling and data analysis. These analyses include data from various major aircraft campaigns such as the Stratosphere Troposphere Exchange Project (STEP); the Airborne Antarctic Ozone Experiment (AAOE); the first and second Airborne Arctic Stratospheric Expeditions (AASE I and II); the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE); the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effect of Stratospheric Aircraft (ASHOE/MAESA); the Tropical Ozone Transport Experiment/Vortex Ozone Transport Experiment (TOTE/VOTE) mission; the Observations of the Middle Stratosphere (OMS) mission; and the Stratospheric Tracers and Atmospheric Transport (STRAT) mission.

ACMAP primarily supports data analysis and modeling studies of tropospheric and stratospheric chemistry, as well as of stratospheric dynamics. Multi-dimensional computational models are heavily used for data analysis, as well as in both retrospective and prognostic modeling studies. ACMAP supports the analysis of datasets on several scales, including balloon profiles, ground-based measurements, the extensive set of aircraft measurements noted above, and the full range of space-based measurements made by NASA and other entities. Among the datasets most extensively analyzed by ACMAP and related NASA data analysis efforts (see below) are the Stratospheric Aerosol and Gas Experiment (SAGE) I and II, the Total Ozone Mapping Spectrometer (TOMS), those aboard the Upper Atmosphere Research Satellite (UARS), and the Solar Backscatter Ultraviolet (SBUV) instruments, as well as those instruments which flew as part of NASA's Atmospheric Laboratory for Applications and Science (ATLAS) series of missions. ACMAP is beginning to support analysis of other data, including that produced from the Global Ozone Monitoring Experiment (GOME) aboard the European Space Agency's ERS-2 satellite.

A major focus of international concern has been (and continues to be) the assessment of the combined effects of past and present emissions of CFCs; the present and future releases of existing and proposed CFC alternatives such as the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs); continued increases in the atmospheric concentrations of the halons (used as fire suppressants) and methyl bromide (CH_3Br); as well as continued growth in the atmospheric burden of CO_2, NO_x, and other gases having significant anthropogenic sources such as N_2O and CH_4. All of these gases play important roles in defining upper atmospheric composition through chemically induced changes in stratospheric (as well as upper tropospheric) ozone and through alteration of the atmosphere's radiative balance. Hence, a corollary program goal is to understand the role of stratospheric ozone in the radiative heating and dynamics of the atmosphere and, thereby, to assess the importance of chemical-radiative-dynamical feedbacks on the meteorology and climatology of the stratosphere and troposphere.

Many of the trace gases in the hydrogen, nitrogen, and halogen chemical families which participate in the chemistry of ozone have been detected in the stratosphere and more detailed information on their spatial and temporal variations is becoming available. Laboratory studies (particularly in the area of heterogeneous reactions) have strengthened our knowledge of the chemical kinetics of stratospheric components, and have provided improved data on the spectroscopy of atmospheric gases for applications to atmospheric measurements of trace species. Current research funding supports specific investigations dealing with the following topics:

- Determination of the distribution of trace gases in the stratosphere, with emphasis on those species which influence the ozone balance.
- Observations of the global distribution of ozone, its vertical profile, and temporal variations. A key initiative in this area is the implementation of a ground-based remote-sensing measurement under the Network for the Detection of Stratospheric Change (NDSC).
- Determination of the geographic distribution and strengths of the sources and sinks for stratospheric compounds. A strong focus in this area is associated with chlorofluorocarbon alternatives, such as the HCFCs and HFCs.
- Improvements in the understanding of atmospheric dynamics and transport processes both by theory and advanced measurement technology, emphasizing the transport of constituents across atmospheric "boundaries" including those between the stratosphere and troposphere, the wintertime stratospheric polar vortex and mid-latitudes, and the tropical and mid-latitude lower stratosphere.
- Measurements of the ultraviolet solar irradiance and its temporal variations at the top of the atmosphere, and the relationship between ultraviolet radiation received at the Earth's surface as inferred from satellite data to that predicted using the top-of-the-atmosphere data and radiative transfer models.
- Laboratory studies in spectroscopy and chemical kinetics relevant to the interpretation of atmospheric measurements and to theoretical simulations of the atmosphere.
- Development of more realistic multi-dimensional models of the stratosphere and troposphere.
- Application of 2-D and 3-D stratospheric models to assess the impacts of changing atmospheric composition. Specific emphasis is being placed on assessing the impact of both subsonic and supersonic aircraft on distributions of stratospheric ozone and other trace constituents.
- Evaluation of theoretical models by comparison with atmospheric measurements.
- Development of new technological ideas, techniques, and instruments for use in stratospheric and tropospheric research.

There were several activities during 1994, 1995, and 1996 that should be highlighted. In general they each involve several facets of the research supported by UARP and ACMAP. These include:

1. **An extended analysis of the data from the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effect of Stratospheric Aircraft (ASHOE/MAESA).** UARP and AEAP have completed a major airborne field campaign, conducted during FY 1994 and early FY 1995 out of NASA Ames Research Center and Christchurch, New Zealand. The main goals of this project were to improve our understanding of the downward trend in total ozone at sub-polar and mid-latitudes, to better understand the role of ozone in global warming, to assess the role of aerosols in perturbing stratospheric chemistry and to directly test the rates of production and destruction of ozone and reactive trace gases over a wide range of latitudes and seasons. The data from this campaign will play an important role in assessing the environmental acceptability of high-speed civil transports (HSCTs).

2. **The Stratospheric Tracers of Atmospheric Transport (STRAT) Mission.** This series of ER-2 and high-altitude (e.g., balloon) deployments has extended the database for stratospheric trace gas distributions and correlations, focusing on mid-latitudes and tropical regions, with the objective of obtaining climatologies of trace gases, chemically active species, and dynamical quantities over at least one cycle of the quasi-biennial oscillation for all seasons. An improved understanding of transport processes, in particular stratosphere-troposphere exchange, will enable us to better assess global-scale transport and predict future distributions of trace gases emitted into the atmosphere, notably those associated with HSCT exhaust in the lower stratosphere. STRAT was initiated in May 1995 with a subset of the instrumentation, and came into full operation in FY 1996 with three separate deployments, and will continue into FY 1997. STRAT is co-sponsored by UARP, the Atmospheric Effects of Stratospheric Aviation (AESA) activity of AEAP, and ACMAP.

3. **Tropical Ozone Transport Experiment (TOTE) and Vortex Ozone Transport Experiment (VOTE).** This aircraft campaign consisted of DC-8 deployments featuring an ozone lidar and a newly-developed methane/water lidar. The mission goal was to examine the extent of production and dispersal of filaments from the tropical and polar vortex regions, which play a significant role in the exchange between polar or tropical and mid-latitude air. DC-8 integration and test flights took place in 1995, and the deployments continued in 1996 (tropical deployment in November/December 1995, Guam; Arctic deployment in January/February 1996, Anchorage, AK, and Keflavik, Iceland).

4. **The Observations from the Middle Stratosphere (OMS) Mission.** The OMS activity provides high-altitude measurements from balloon-borne instruments as a partner with STRAT and other missions. High-altitude measurements will be used in conjunction with the ER-2 observations in the Northern Hemisphere, covering a range of latitudes from the tropics to 65°N. These measurements are essential for defining the transport and transport rates of trace gases, particularly in the tropics and between the tropics and middle latitudes. These transport rates define the spread of emissions such as HSCT exhaust to the Southern Hemisphere or to higher altitudes (e.g., the ozone source region), the spread of volcanic debris in the stratosphere, and the atmospheric lifetimes of various anthropogenic pollutants. Construction, modification, and testing of the OMS instrument suite were completed during FY 1996 with deployments continuing into FY 1997.

5. **Continuing Implementation of the Network for the Detection of Stratospheric Change (NDSC).** The NDSC is a set of high-quality research stations for observing and understanding changes in the physical and chemical state of the stratosphere that are complemented by secondary stations and satellite measurements and are coordinated with other networks. NASA UARP has continued to support the development of the state-of-the-art instrumentation for these stations. A fully implemented NDSC will serve as a focal point for future ozone trend determinations and such analyses have already been initiated using data from several stations.

6. **Continuing analysis of total column ozone and data on vertical distribution of ozone**. There have been appreciable changes in the sources of space-based measurements of atmospheric ozone since the 1994 report. The Total Ozone Mapping Spectrometer (TOMS) instrument which flew aboard a Russian Meteor-3 spacecraft failed in December 1994, and there was a gap in TOMS measurements until the recent launches of new TOMS instruments

aboard the US Earth Probe spacecraft on 2 July 1996 and the Japanese ADEOS spacecraft on 17 August 1996. An additional SBUV/2 instrument was launched in December 1994, and the European Space Agency launched its GOME instrument in mid-1995. The SBUV/2 instrument aboard the NOAA 11 spacecraft failed during this time. There have been three flights of the Shuttle Solar Backscatter Ultraviolet Instrument (March 1994, November 1994, January 1996) since the last report. A highlight over the past three years has been the development of a new TOMS dataset (Version 7), which includes several important corrections over the previous version. These TOMS data have also been shown to provide information on the distribution of ultraviolet radiation reaching the Earth's surface, and global trend studies have been carried out for this new data product, which has been validated by comparison with ground-based instruments.

7. **Dramatic increase in availability of space-based atmospheric chemistry datasets.** There are now more than five years of data available from UARS (launched in September 1991), which include information on the distribution of most important upper atmospheric trace constituents, as well as top-of-the-atmosphere total solar irradiance and spectrally-resolved solar irradiance, and information on upper atmospheric winds and particle input into the atmosphere. The final flight of the ATLAS payload took place in November 1994. These data have been extensively analyzed, especially in regards to their information about the distribution of halogen-containing species in the stratosphere. Conclusive evidence was obtained indicating that the major portion of stratospheric halogens (chlorine, fluorine) is derived from industrially produced halocarbons, and that the increase in the stratospheric burden of these compounds over nearly a decade is consistent with the increase in halogen-containing source gases measured at the Earth's surface.

8. **Significant increase in knowledge of the global distribution of stratospheric aerosols and their effects on ozone distributions.** There has been a significant decrease in the abundance of stratospheric aerosols since the issuance of the last report, as the enhanced aerosol due largely to the June 1991 eruption of Mt. Pinatubo in the Philippines has decayed. Concentrations of stratospheric aerosols are now getting close to their pre-Pinatubo levels. During the last few years, continued monitoring of stratospheric aerosol levels through the SAGE II instrument, balloon-borne instruments, and ground-based lidar networks has provided significant information on aerosol distributions, and aircraft and balloon measurements have provided important information on the size distributions of stratospheric aerosol particles. Space-based infrared measurements from ATLAS and UARS provided information on the distribution and composition of stratospheric aerosols. High-latitude measurements of polar stratospheric clouds (PSCs) are being continued by the Polar Ozone and Aerosol Monitor (POAM II) instrument built for the US Department of Defense. POAM II helps to fill the gap created by the inability of the Stratospheric Aerosol Monitor (SAM II) instrument to observe high latitudes due to degradation of the Nimbus 7 orbit. Numerical calculations have shown clearly that the year-to-year variation in aerosol distributions can have a significant effect on ozone amounts. TOMS data were also shown to have information about stratospheric aerosol distributions during times of high volcanic aerosol loading, as well as information about the distribution of ultraviolet-absorbing tropospheric aerosols.

9. **Participation in International Assessments.** The most recent version of the international *Scientific Assessment of Ozone Depletion* was completed in 1994 and issued in 1995. This effort was coordinated by NASA and the National Oceanic and Atmospheric Administration (NOAA) and co-sponsored by the United Nations Environment Program, the World Meteorological Organization, and the United Kingdom Department of the Environment. UARP and ACMAP investigators also participated in updating the report to the Inter-governmental Panel on Climate Change (IPCC), including both the 1994 interim assessment on radiative forcing and the full 1995 assessment (Working Group I). UARP and ACMAP investigators contributed heavily to the recent 1995 Scientific Assessment of the Atmospheric Effects of Stratospheric Aircraft, led by NASA's Office of Aeronautics.

While the material in this report focuses on the work supported by UARP and ACMAP, it should be noted that there is a significant amount of effort carried out by NASA related to atmospheric ozone which is not directly addressed in this report. This includes work supported through the following programs:

- Earth Observing System (EOS) - Both instrument development and theory and data analysis work are supported through this program. A major augmentation was made to this program in 1996 to allow for better consideration of the interaction between atmospheric chemistry and climate issues.
- Mission Operations and Data Analysis (MO&DA) - This includes support for spacecraft operations, data reduction, and science analysis for data from UARS, SAGE, TOMS, and SBUV instruments. Science data analysis is supported through Guest Investigator Programs and/or Science Teams through the Science Division of NASA's Office of Mission to Planet Earth.
- Flight Systems - This includes support for the development of instruments to fly aboard US and other spacecraft, including the recently launched TOMS instruments (the final TOMS instrument is scheduled to fly in 2000 aboard a Russian spacecraft), the planned SAGE instruments (1998 on a Russian spacecraft, approximately 2001 aboard the International Space Station, and an additional flight to be determined), and several atmospheric chemistry and solar irradiance instruments to be flown as part of NASA's EOS program.

FIELD MEASUREMENTS

A. BALLOON-BORNE IN SITU MEASUREMENTS
B. BALLOON-BORNE REMOTE MEASUREMENTS
C. GROUND-BASED MEASUREMENTS
D. AIRCRAFT-BORNE MEASUREMENTS
E. ROCKET-BORNE MEASUREMENTS

A. Balloon-Borne In Situ Measurements

Lightweight Airborne Chromatograph Experiment (LACE)

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Research Objectives

The Lightweight Airborne Chromatograph Experiment (LACE), a new instrument for the Observations of the Middle Stratosphere (OMS) component of the Stratospheric Tracers for Atmospheric Transport (STRAT) mission, is designed to measure chlorofluorocarbon-11 (CFC-11), CFC-113, and sulfur hexafluoride (SF_6) from a balloon platform. CFC-11 represents about 25% of the total organic chlorine budget. The remainder can be estimated from the correlation of CFC-11 with other organic species, as found in recent ACATS-IV stratospheric datasets or as computed in 2-D models of the atmosphere [Woodbridge *et al.*, 1995]. The measurement of sulfur hexafluoride (SF_6) permits the calculation of the mean age of the air mass because of its long atmospheric lifetime (~3200 yr) and linear growth with time (~6.7 % yr^{-1}) [Geller *et al.*, 1996]. LACE is a smaller version of the ACATS-IV instrument flown on the ER-2 aircraft [Elkins *et al.*, 1996]. The key differences are more frequent sampling (one sample every 70 seconds), higher altitude sampling (up to 32 km or higher), less weight and space (less than 50 kg), and at the expense of fewer molecules measured than the ER-2 version. The instrument comprises two separate gas chromatographic (GC) channels, each incorporating an electron capture detector (ECD). On channel 1, CFC-11 and CFC-113 are separated from air using a silicone column and, similarly, SF_6 is separated from air on a molecular sieve column on channel 2. A sampling period of 70 seconds is made possible with the use of a 2-position, 10-port gas sampling valve that allows the last half of the chromatogram to be folded back into the next one. Otherwise, the chromatographic separation of the peak of interest from air takes 120 seconds. We have had

two successful balloon flights: one test flight in May 1996 and one science-ready flight in September 1996.

Summary of Progress and Results

The first LACE balloon flight did not acquire science quality data due to a small technical problem with the pumps. On the second flight, all instrument functions were satisfactory. Figure 1 shows vertical profiles of CFC-11 and SF_6 from this flight over Ft. Sumner, New Mexico on 21 September 1996. For the most part, the mixing ratios of both tracers for the ascent and descent agree indicating that balloon outgassing is not a serious problem. The oldest air sampled is about 5.5 to 6 years old using the growth of SF_6 in the troposphere. Another interesting feature is that the mixing ratios at tropopause yield about 0.5 to 0.7 year older air than the global tropospheric mean values at the ground. This difference may be the result of the large interhemispheric difference in mixing ratios observed at ground levels. As an additional benefit of this research,

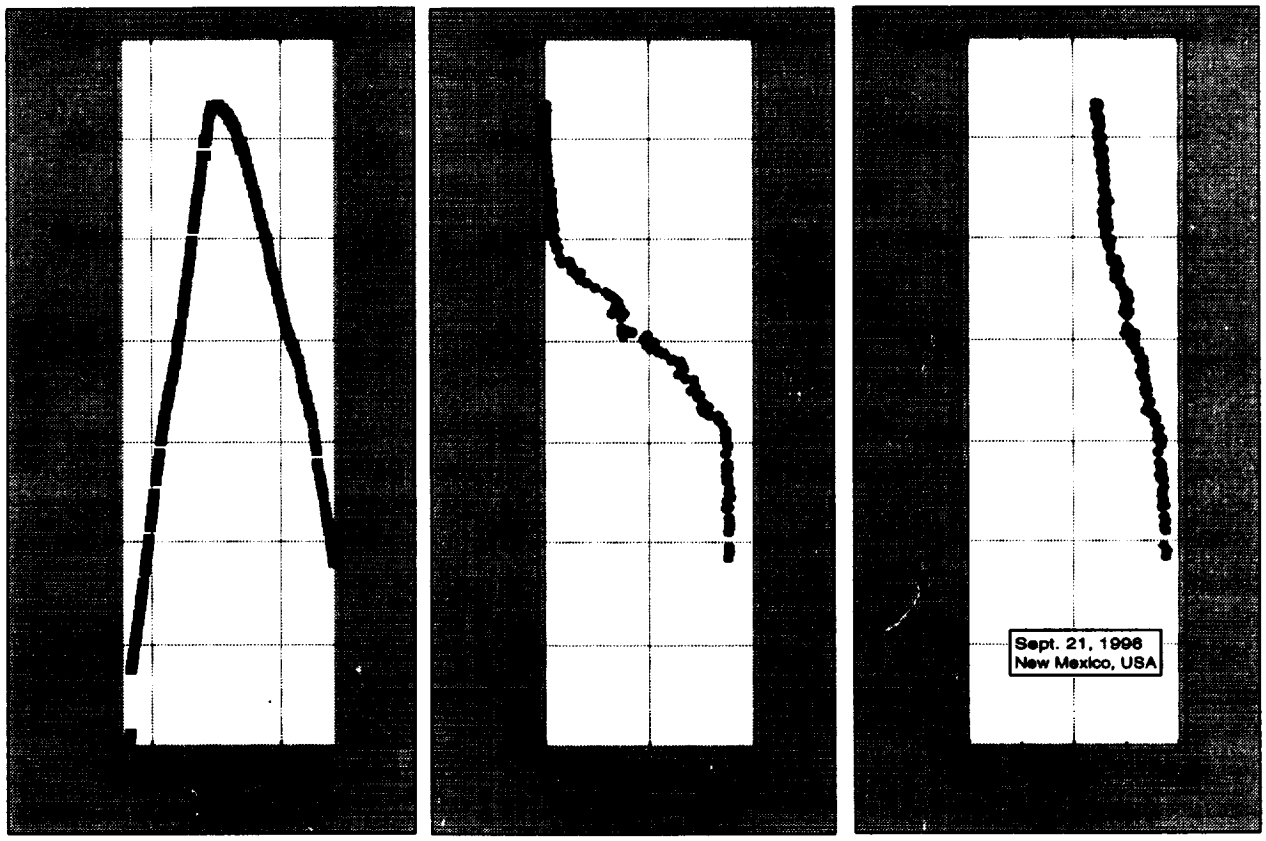

Figure 1. Altitude (km) versus time (s), altitude versus mixing ratios of CFC-11 (ppt), and altitude versus mixing ratios of SF_6 for the OMS balloon flight of 21 September 1996. Darker circles indicate ascent and lighter circles indicate descent. Note that mixing ratios of CFC-11 approach zero at 32 km, while mixing ratios of SF_6 do not come close to zero and shows its growth in the atmosphere. Data presented here are preliminary.

we will probably be able to calculate tropospheric mixing times from the data if we use precise ground base station data.

In the tropical lower stratosphere, the correlation slopes between CFC-11 and N_2O, CFC-11 and CH_4 are different from that observed in polar or mid-latitudes. This difference indicates the failure of the 'global diffuser' model [Plumb and Ko, 1992] for transport in the lower tropical stratosphere and suggests that the 'tropical pipe' model is more representative [Plumb 1995]. Volk *et al.* [1996] used ER-2 measurements up to altitudes of 20 km to determine that the tropical pipe is leaky with about 45% of the tropical stratospheric air originating from the mid-latitudes. LACE measurements will allow this difference to be studied at higher altitudes. Reproducing the latitude-height distribution of the mean age for air parcels in the lower stratosphere, as determined from SF_6 measurements, will be a strong test of atmospheric models and will clarify further how representative 'diffuser' and 'pipe' transport models are. Establishing the details of transport between mid-latitudes and the tropics is an essential component in the environmental assessment of future aircraft operations. LACE was configured first on a balloon platform and can be modified at a later date for use on remotely piloted aircraft.

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Publications

None

Balloon-Borne Ozone Measurements at Hilo, Hawaii during MLO_3

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Research Objectives

At the Network for Detection of Stratospheric Change (NDSC) site at Mauna Loa, Hawaii (MLO) several measurement systems are being used to measure the ozone profile in various atmospheric altitude ranges. The balloon-borne ozone sonde has been added to the complement of instruments measuring the ozone profile at MLO primarily focusing on observing the lower stratosphere and troposphere. The objective of this research is to compare the ozone profile obtained from the electrochemical ozonesonde with that obtained from ground-based lidar, microwave, and Dobson spectrophotometer instrumentation. The sondes were also intercompared with the Upper Atmosphere Research Satellite (UARS) and Stratospheric Aerosol and Gas Experiment (SAGE) II ozone profiling sensors.

Summary of Progress and Results

Eighteen successful balloon launches were carried out during August 1996 from Hilo, Hawaii. Six of these soundings included "triple" packages in which three individual ozone sensors were flown on a single balloon. The "triple" packages and the accompanying telemetry and processing computer hardware and software were developed specifically for this campaign. The results from the "triple" sondes showed that the ozone sondes were able to achieve a high degree of precision in both the stratosphere and troposphere with an average deviation of the triples of 5% of the mean. In the altitude region above 35 km the precision was somewhat worse with the average standard deviation rising to about 10% of the mean.

Each of the balloon soundings was carried out with a concurrent lidar and microwave ozone profile. It was found in the region at and above the ozone partial pressure maximum (~25 km) that the ozonesonde gave ozone amounts about 10% higher than the other observations. At the time of the intercomparison the cause of this difference was unknown. Subsequent tests carried out in the laboratory showed that the sensitivity of the reactant in the sensor (potassium iodide

solution) depends somewhat on the solution concentration. The original solution concentration (1%) appears to be slightly too concentrated based on comparisons of sensors using different concentrations with a calibrated ultraviolet absorption ozone monitor. As a result of the intercomparison and the related laboratory work, it will be possible to correct ozonesonde data obtained over the past 10 years and in the future to obtain data with greater accuracy.

In addition to the balloon ozone soundings, the work of the intercomparison referee was also carried out as part of this research effort. Each day all the ozone vertical profile information was submitted to the referee such that each group did not have a knowledge of the other groups' results. The preliminary results of the intercomparison were presented at the NDSC meeting and the American Geophysical Union meeting in Fall 1995. Final results are being prepared for publication and presentation at the 1996 Quadrennial Ozone Symposium.

Publications

None

Argus: A CH_4 and N_2O Dual-Channel Tracer Instrument for Stratospheric Dynamics Studies

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Research Objectives

The Argus instrument, a tunable-laser, infrared spectrometer, was designed to measure the long-lived tracers methane and nitrous oxide in the stratosphere up to altitudes of 30 km. The ratio of these two tracers as a function of altitude provides important information on the dynamics of different regions of the stratosphere: the surf zone, the tropical pipe region, and the polar region distinguished by its strong winter vortex isolation.

Summary of Progress and Results

The NASA Ames Research Center Argus instrument was flown on the ER-2 aircraft in October 1995 in a test mode preparatory to its deployment on a balloon in 1996. The information gleaned from two flights allowed us to design the thermal control system for the instrument in its balloon version.

In June 1996, the Argus instrument was flown to 32 km altitude on a balloon from Ft. Sumner, New Mexico (34°N) the site of the NASA National Scientific Balloon Facility. The instrument performed well and returned a reasonable profile of N_2O over much of the balloon altitude range sampled on that flight. The methane channel was not operational on this first flight.

The data acquired in the Ft. Sumner June balloon flight pointed the direction for several instrument improvements that have been incorporated into Argus preparatory to a September balloon science mission in Ft. Sumner, followed by a tropical tracer mission in Brazil in November 1996.

Publications

None

Balloon-Borne *In Situ* Ozone Measurements

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Research Objectives

The research conducted under this RTOP obtains profiles of ozone in the Earth's stratosphere and troposphere using a dual channel UV photometer flown aboard balloons. The high accuracy and precision ozone measurements address a number of objectives, in addition to simply providing ozone profiles: (1) validation measurements for other instruments aboard balloons and satellites; (2) measurements at high spatial resolution complement the other predominantly remote sensing instruments; (3) a comprehensive suite of data for testing photochemical models is provided by the combined instruments; and (4) ozone is one of a number of tracer measurements for studying transport. Balloon flights are supported by the JPL Balloon Flight Support Group.

Summary of Progress and Results

Since the launch of UARS in Fall 1991, a major activity for the Ozone Photometer has been participation in the UARS Correlative Measurements Program, making 11 flights in the just over 3 years of the CMP. In the CMP, the balloon instruments of the UARP have been combined in a number of configurations, and have provided correlative profile data for all of the chemical species measured by UARS. The Ozone Photometer has flown, during the CMP, with all of the UARP remote sensing instruments, providing a useful cross check among them. During this reporting period, the Photometer flew from Ft. Sumner, New Mexico in Fall 1993 with Toon/Stachnik/Pickett; in Spring 1994 with Toon/Traub; and in Fall 1994 with the Murcray emission FTIR. In addition, two flights were made from Kiruna, Sweden, as part of the European SESAME campaign (although the Ozone Photometer was not an official participant) in February 1994 with Stachnik's Submillimeter Limb Sounder and the KFA-Julich whole air sampler and in February 1995 with the University of California, Irvine (Toohey) ClO instrument and the KFA-Julich whole air sampler.

The Fall 1993 flight included measurements of the full suite of radicals, precursors, reservoirs and tracers, and a detailed analysis of that data is being carried out in conjunction with the

photochemical modeling of Salawitch and co-workers. It also provides one of the most comprehensive sets of ozone measurements we have, including the photometer, MkIV, and SLS on the balloon, and UARS MLS and HALOE, as well as SAGE II. The comparisons show generally excellent agreement, albeit somewhat complicated by measurements across different airmasses. Also, with the decline of the Pinatubo aerosol, and the cloud-free conditions, the MkIV was able to make measurements extending well into the troposphere (within a few km of the surface). The agreement of MkIV and *in situ* ozone is excellent (much better than expected) and is helping to determine the extent to which the MkIV can provide other tropospheric measurements, for example, nitrogen oxides.

The Kiruna flights provide a valuable augmentation to our ER-2 datasets, using a virtually identical instrument to get ozone profiles to much higher altitudes (near 15 mb). The two winter profiles clearly show the ozone mixing ratio continuing to increase with altitude. In the polar ozone ER-2 campaigns, the descended air encountered within the vortex (lower N_2O), did not show significant increases in ozone, with one plausible explanation being that the air was from "above" the ozone maximum. That seems less likely in view of the balloon data. The second Kiruna flight was even more dramatic, finding air with high levels of ClO (1200 pptv) and reduced ozone (about 20% less than surrounding air) at an altitude just above that typically sampled by the ER-2, providing the first direct *in situ* observation in the Arctic of the ClO-O_3 anti-correlation that had been seen in the Antarctic. Further analysis of the data from that flight is underway.

The UV Photometer was flown as part of the OMS *in situ* tracer gondola, with a flight from Ft. Sumner in June and another planned for September 1996, prior to the Brazil deployment in November. Comparison of O_3 with ALIAS II N_2O for the June flight shows good agreement with the ER-2 data in May 1995 and July 1996 in the overlap region, but varying agreement with several MkIV remote-sensing datasets from earlier flights (May 1994 sunset, and September 1993 sunset and sunrise), emphasizing the need for close coincidence in such intercomparisons. The OMS data overlay the ER-2 rather well, and of course, don't show the large spread that's in the wide latitude range of the May 1995 ER-2 data. The MkIV comparisons show reasonable agreement at ER-2 altitudes but significant differences at higher altitudes. The MkIV September 1993 data show dramatically different relationships for the sunset and sunrise observations (12 hours, and about 1000 km apart): at N_2O = 175 ppbv, O_3 changes from 3 to 7 ppmv in the two. Interestingly, the OMS data seem to fit the sunrise curve up to about O_3 = 3.5 ppm and then fit the sunset curve better for the higher altitude portion: perhaps the different airmasses indicated by the 2 MkIV profiles were encountered by the OMS flight at different altitudes. The OMS dataset provides several important observations relevant to the ER-2 data: (1) the ER-2 samples a very small portion of "parameter space;" (2) the fairly tight, linear correlations seen in the ER-2 data cannot be simply extrapolated outside that range (without great care, and appropriate caveats); and (3) ozone is not simply a tracer, and its relatively short photochemical lifetime needs to be considered. The OMS flight ozone data are also being provided to the ESA ERS-2 GOME team, as our first opportunity for a validation flight since the ERS-2 launch.

This RTOP also supports the participation of Margitan as co-PI for the ER-2 ozone instrument (see Proffitt's Aircraft Ozone Photometer summary). In this period, that included the Fall 1993 SPADE follow-on mission, the 1994 ASHOE/MAESA deployments, and the 1995-1996 STRAT campaigns.

During this time, Margitan also served as the Balloon Measurements Manager for the UARS CMP. Additionally, under a NASA Small Business Innovative Research activity, Physical Sciences, Inc. is building a next generation version of the ozone photometer, approximately one-third the weight of the present balloon instrument, for delivery in 1997.

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Water Vapor Measurements of the Middle Stratosphere Using a Balloon-Borne, Frost-Point Hygrometer

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Research Objectives

In order to understand the dynamics and chemistry of the middle stratosphere above the region generally accessible by high flying aircraft, the Observation of the Middle Stratosphere (OMS) balloon package is being developed to measure key atmospheric constituents in the 20 to 30 km altitude range. The complement of instruments being deployed for the OMS campaigns includes an in situ water vapor sensor being developed and built under this task. The sensor is of the chilled mirror design, which has been extensively used in stratospheric applications. Water vapor plays a significant role in the chemistry of this region and is likely changing as a result of increasing levels of methane in the atmosphere [Oltmans and Hofmann, 1995]. In addition, the water vapor distribution in the lower stratosphere reflects the processes that exchange material between the troposphere and stratosphere, particularly in the tropics, and is sensitive to the tropopause temperature at which water vapor enters the stratosphere [Vömel *et al.,* 1995]. Campaigns are to be carried out at a mid-latitude (Ft. Sumner, New Mexico) and tropical location (Brazil) in September and November 1996, respectively.

Summary of Progress and Results

Funding for this project was received during the first quarter of 1996. Design of the OMS instrument was done based on the concept successfully used in smaller balloon packages on which the water vapor instrument was the sole component. The chilled mirror technique measures the temperature of a mirror, which is controlled such that the mirror maintains a small and constant layer of frost coverage. Under these conditions the mirror temperature is the frost-point temperature of the air passing over the mirror and is a unique measurement of the water vapor content of the air. A heater controlled by an optical-electronic circuit heats the mirror against a cryogenic bath to maintain the mirror temperature.

The instrument that has been built for the OMS balloon package is mounted on arm extending approximately 3 m from the main gondola. This is necessary to minimize the contamination from the gondola since *in situ* water vapor measurements are easily compromised by outgassing from the instrument itself or surrounding materials. Credible water vapor measurements can be obtained in the

stratosphere from a balloon package only on balloon descent. Because of the exposed position of the water vapor instrument on the outrigger, all of the key components have been duplicated in a second instrument so that a second balloon flight can be accomplished within a short period of time. The water vapor package includes an onboard data logger, a feed to the gondola telemetry, and several commands for activating the instrument and providing control of various test functions.

A test flight was carried out in Ft. Sumner, New Mexico in June 1996. Several shortcomings in the data system were found and these have been corrected. Several adjustments to the balloon descent profile characteristics are also being made to help avoid contamination of the air sample.

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Publications

None

Measurements of ClO and BrO in Support of the SESAME Campaign

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Research Objectives

A new instrument to measure ClO and BrO in the lower-to-middle stratosphere was deployed on scientific balloons during the Second European Stratospheric Arctic and Mid-latitude Expedition, (SESAME) in February and March 1995. Two launches took place from Kiruna, Sweden, with the objectives of (a) characterizing the performance of a low-cost, lightweight design for balloons and autonomous aircraft, and (b) obtaining a high-accuracy, high-resolution profile of ClO and BrO for intercomparison with other instruments simultaneously deployed on the ground, satellite, and by balloons and aircraft. All of the proposed objectives were met, including the first high-altitude (above 20 km) *in situ* profile of BrO and near-coincident measurement for the MLS instrument on the UARS satellite. The instrument performed flawlessly on the first flight, and during the second, extensive diagnostics proved that the instrument is robust for future measurements from aircraft and balloons.

Summary of Progress and Results

A new instrument designed to measure CIO and BrO with part-per-trillion (10^{-12}) precision and high accuracy (20-25%) was built at UCI with funding from the University of California, The Methyl Bromide Global Coalition, and the National Science Foundation. This instrument is lightweight (less than 40 kg) and uses many commercial parts in an effort to keep the equipment costs below $100,000. Funds from NASA under this grant were used to support travel to Sweden for key personnel to participate in the SESAME campaign, organized by the EC, and for extensive post-flight data analysis efforts. Several broad objectives were met by two balloon flights of the instrument in February and March 1995.

- The thermal, optical, mechanical, and electrical performance was near-perfect on the first flight of the instrument. The only issue was frost buildup on the photomultiplier tube window during ascent on account of excess water vapor in the ultra-zero air used to keep the optics dry during flight. This problem was the result of a contaminated regulator used to fill the on-board air supply bottle, and was alleviated by *in situ* warming of the instrument following ascent into the warmer middle stratosphere.

- The precision of the BrO measurement was improved ten-fold over the most precise previous design that had been demonstrated by the PI on the NASA ER-2 during the AASE II campaign. This was achieved by improving the spectral characteristics of the absorption cell used to isolate bromine atom resonance in the detection cell.
- An intercomparison with the ClO measurement on UARS was obtained with high spatial and temporal coincidence. This represents the first intercomparison of the microwave emission (remote) and chemical conversion (*in situ*) techniques over the altitude range where both instruments have high signal-to-noise ratios. The preliminary results indicate that the shape of the two profiles agree well, but the absolute abundance measured by UARS is greater at 46 hPa, perhaps due to lack of a constraint in the ClO abundance at lower altitudes (100 hPa). Further analysis is pending.
- The simultaneous measurements of ClO, BrO, ozone, particles, and source gases on the first flight will significantly improve our understanding of the photochemistry governing ozone loss at high latitudes in wintertime. A manuscript reporting the first results has been submitted for publication in a special issue of the *Journal of Atmospheric Chemistry*. This work shows that production of Cl_2 and OClO at night might occur at some altitudes where air has warmed above 225 K as a result of the disproportionation of ClO. These results have great implications for interpretations of the BrO abundance from slant-column measurements of OClO.

Publications

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Electrochemical Concentration Cell (ECC) Ozonesonde Calibration and Launch

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Research Objectives

The vertical distribution of ozone concentration is studied for a number of sites through the use of well calibrated electrochemical concentration cell (ECC) ozonesonde instruments. Computer-controlled simulations of ozone concentration vs. atmospheric pressure are performed to examine characteristics of the ECC instrument prior to actual flight. Simulations and well-controlled preflight preparation of the ECC enable reasonable estimates of instrument error to be determined to the higher altitudes, where the ECC reaches its measurement limit, and to be removed. These calibrated and well understood instruments have been used in obtaining vertical ozone measurements from Antarctica, Wallops Island, Brazil, and other locations as required. Because of the advancing nature of new technology new tests are constantly being contrived that have led to improved measurement capability. It is important that comparisons with other instruments, *in situ* and remote, be periodically conducted and results made known to the science community. Only in this manner can the future of atmospheric contamination be accurately predicted and relieved as the situation demands.

Summary of Progress and Results

During FY 1994, ECC ozonesondes were released bi-weekly from Wallops Flight Facility and during FY 1995, forty vertical ozone measurements were obtained from Palmer Station, Antarctica, between mid-September and November 1994. The Antarctic data were obtained using digital ozonesonde instruments, the first of this instrument design to be flown by NASA Wallops. The lowest ozone value reported from Antarctica was 0.98 mb at the pressure level of 78 hPa. This measurement coincided with a drop in the total ozone overburden to a value of 128 Dobson Units reported at Faraday, Antarctica. During July 1995, ozone project management at Wallops Flight Facility initiated weekly ozonesonde observations. A large number of correlative vertical profiles were obtained in conjunction with the Halogen Occultation Experiment (HALOE) remote instrument on the Upper Atmosphere Research Satellite (UARS). During FY 1996, weekly measurements continued at Wallops Flight Facility along with supplemental special correlative observations made in conjunction with the HALOE experiment. In a continuing effort to improve vertical ozone measurements comparisons between various balloon-borne instruments are important. During May 1996, a special test was carried out between the Brewer-Mast type ozonesonde in use at the Swiss Meteorological Institute, Payerne, Switzerland and the ECC

instruments used by NASA. Preliminary results indicate that the integrated ECC measurements giving total ozone overburden values agreed within less than 2 percent of the Dobson Spectrophotometer operated by the Swiss. This is slightly better than the comparisons made with the Dobson at Wallops Flight Facility where agreement within less than 4 percent is usual. The Brewer-Mast instrument also is believed to estimate lower amounts of ozone concentration at levels above the ozone peak (~16 hPa).

NASA Wallops Flight Facility, based on the measurements and test made over the past year has begun a review of ECC calibration procedures that, in combination with the new digital instruments making data available at 2-second intervals, is hoped to improve the quality of the NASA ozonesonde measurements even further.

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Balloon-Borne *In Situ* ALIAS-II Instrument

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Research Objectives

The Aircraft Laser Infrared Absorption Spectrometer (ALIAS-II) task has as its primary objective the collection of data on the concentrations, distributions, and variabilities of the minor and trace species in the stratosphere and troposphere. The *in situ* laser absorption spectrometers ALIAS (ER-2) and ALIAS-II (RPV, balloon) provide measurements of several gas concentrations as part of multi-instrument aircraft and balloon payloads flown for NASA missions, and for satellite correlative measurements (e.g., Upper Atmospheric Research Satellite (UARS)). The instruments use tunable diode lasers in the 3-10-μm wavelength region to measure gas concentrations in multi-pass optical cells either contained in a flow vessel (ALIAS) or in an open-path deployed cradle (ALIAS-II). The instruments have demonstrated capability for: N_2O, CH_4, HCl, CO, and NO_2, at the tens-of-parts-per-trillion levels, with capability to measure other gases within the 3 to 20-μm wavelength region; ALIAS is a 4-channel instrument, ALIAS-II is a 2-channel instrument.

Summary of Progress and Results

The Aircraft Laser Infrared Absorption Spectrometer (ALIAS-II) instrument is a lightweight (50 lbs.) two-channel version of the ER-2 ALIAS instrument, and was originally built in 1994 specifically for Perseus-type RPV platforms, with an open-path sampling from fuselage to wing. This instrument was modified in 1995 for its participation in the ballooning component of the Stratospheric Tracers of Atmospheric Transport (STRAT) mission of 1995/1996. The ALIAS-II instrument has been configured to measure N_2O and CH_4 simultaneously and, in preparation for the balloon test flights, successfully underwent a full thermal-vacuum test at JPL in April 1996.

In support of the Observations of the Middle Stratosphere (OMS) component of STRAT, a multi-instrument balloon payload was integrated and flown for the first time in May 1996 from Ft. Sumner, New Mexico in what proved to be a highly-successful flight for the ALIAS-II instrument. High-quality profiles of both N_2O and CH_4 were obtained on ascent and descent, and no instrument damage resulting from an excellent landing. The tracer profiles show that the test flight sampled predominantly mid-latitude air, a situation noticeably different from the May 1993 SPADE flights. The "fold" in tracer mixing ratios seen by Toon *et al.* in the MkIV data was also clearly visible.

The ALIAS-II instrument is now ready for deployment to Ft. Sumner in September 1996 and Brazil in November/December 1996 in a continued contribution to STRAT, and is expected to participate in the 1997 POLARIS mission. This two-channel spectrometer with its open-path sampling may readily be used to measure the gas combinations: HCl, NO_2, and CH_4; or CO and CH_4; or N_2O and CH_4, depending on the scientific priorities.

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A Lightweight High-Precision Instrument for Atmospheric Carbon Dioxide Measurements

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Research Objectives

The objective was to build a lightweight (less than 45 kg) instrument for measuring concentrations of carbon dioxide in the stratosphere, using observed variations to determine rates of atmospheric transport on global scales. An airborne instrument with the precision required for such measurements, better than +/-0.1 ppm, has been deployed by this group of investigators since 1992 on NASA's ER-2 aircraft. Originally the platform for these observations was intended to be a Remotely Piloted Aircraft (RPA) as part of the Environmental Research Aircraft and Sensor Technology (ERAST) program, but the platform did not emerge. However, an urgent need was identified for this instrument on the small balloon payload planned for high altitude observations during the Observations of the Middle Stratosphere (OMS) program, hence an instrument was built for this platform.

Summary of Progress and Results

The lightweight instrument was constructed (weighing less than 35 km) and deployed in an engineering test flight from Fort Sumner, New Mexico in June 1996. Several modifications were required from the original ERAST design, including a high compression pump and advanced heat management to allow operation to 10 mb. Interfaces and software for telemetry control and data output had to be added.

June/July activities: Instrument performance was excellent in the test flight, including calibration data at all flight levels, although a valve malfunction limited atmospheric observations to a few minutes of data. We expect that performance specifications will be surpassed at all flight levels.

Plans for August/September: Science flights for this instrument are scheduled for September 1996 from Fort Sumner, and December 1996 from Juazeiro do Norte, Brazil. Preliminary information on the first science results should be available after 1 October 1996.

Publications

None

High-Altitude NO and NO_y Measurements Using a New, Lightweight Chemiluminescence Instrument

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Research Objectives

Field measurements of NO and NO_y were proposed, using a new lightweight dual-channel NO/NO_y instrument to investigate processes regulating NO_x, NO_y and ozone in the lower and middle stratosphere. The measurements were intended to be part of the HSRP 1994 field program and to complement ER-2 measurements planned for the Airborne Southern Hemisphere Ozone Experiment (ASHOE). Altitudes above the operational envelope of the ER-2 were targeted in the tropics and middle latitudes. A fully operational 35 kg instrument was planned to be tested in the stratosphere and incorporated into a lightweight payload with ClO, BrO, ozone, T and P and a tracer instrument (probably a tunable diode laser spectrometer currently under development) on the Perseus A.

Summary of Progress and Results

The proposed stratospheric flight instrument was to measure NO using chemiluminescence and NO_y by catalytic conversion to NO followed by chemiluminescence. The instrument was designed, components and sub-assemblies were extensively tested, but it has not flown because Perseus A did not emerge, nor did any other RPA platform.

During the development, we performed extensive laboratory studies aimed at optimizing the detection methods and undertook detailed investigations to characterize the NO_y catalytic conversion process over a broad range of conditions (including those relevant to the current controversy surrounding tropospheric NO_y measurements). We also made significant progress in developing alternative detection schemes.

NO Chemiluminescence Detection

We fabricated and tested several new designs for the chemiluminescence cell. The final design has a higher sensitivity, lower zero artifact (in the lab), and lower weight (by a factor of 5) than previous cells. Kinetic modeling of the chemiluminescence cell was undertaken, allowing

optimization of the detector performance within the power and gas-consumption constraints applicable to a range of operational scenarios.

NO_y Catalytic Conversion

Using the NO_y species NO, NO_2, HNO_3, and isopropyl nitrate and the potential interferences HCN, CH sub 3CN, NH sub 3, and N_2O conversion efficiencies as a function of reducing-agent concentration with both H sub 2 and CO; © the effect of humidity and O_3 on conversion efficiency; (d) loss of NO in the catalyst; and (e) the efficacy and suitability as catalytic converters (or inlets) of 24 k gold, 18 k gold, gold doped with 1% cobalt, silver, platinum, stainless steel, and quartz. The most significant results were the discovery of a gas-phase process that contributes to the conversion of HNO_3 to NO and the identification of conditions that produce oxidizing sites on/in the catalyst, allowing HCN, CH_3CN, and NH sub 3 to be converted to NO with high efficiency. We have submitted a manuscript for publication that provides a detailed description of these measurements and discusses their implications for *in situ* measurement of atmospheric NO_y (including recommendations for performing measurements using catalytic conversion).

New Directions

Laser-induced fluorescence (LIF) is a highly sensitive and specific spectroscopic technique for detection of a number of small molecules, including NO. The size, weight, complexity, and power requirements of existing laser systems used to generate the required UV radiation have prevented LIF from being widely applied to field measurements. In collaboration with Lew Goldberg of the Naval Research Laboratory in Washington, DC, we investigated using semiconductor lasers to power a compact, lightweight, electrically efficient (low power consumption, low heat generation), solid-state, inexpensive sources of tunable, narrow-bandwidth UV radiation to be used for LIF. We frequency-quadrupled the output of a high-power diode laser to generate tunable light near 215 nm, the wavelength required for NO LIF. These pilot studies have been published and led to the submission of a patent application. We recently received a grant from the NSF to continue this research.

Publications

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B. Balloon-Borne Remote Measurements

Balloon-Borne Infrared Measurements

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Research Objectives

The objectives of this program are to measure concentrations of trace gases in the upper troposphere and stratosphere using infrared instrument, and to improve the instruments and analysis techniques used for the measurements. Our current instruments include: the very high spectral resolution solar absorption spectrometer system (0.003 wavenumber resolution); a high spectral resolution, cryogenically cooled grating spectrometer that observes the infrared emission from the atmosphere itself; and several Cooled Atmospheric Emission Spectral Radiometers (CAESRs) which are small, light weight emission spectrometers for piggy-back or hand launched balloons. Data from these instruments was compared with UARS observations during the correlative measurements program, and flights will provide current atmospheric measurements referenced to the UARS era.

Summary of Progress and Results

CAESR instruments were flown piggy-back on three flights from Kiruna, Sweden as part of the European SESAME (Second European Stratospheric Arctic and Mid-latitude Experiment) campaign. This provided an opportunity to compare HNO_3 (nitric acid) altitude profiles from CAESR and a solar occultation instrument; the profiles were within 10% between 12 and 30 km, which is well within the combined error bars.

Nine small balloon flights were made from McMurdo, Antarctic with CAESR hand-launched balloon systems during 1994. The flight operations were very successful, and all payloads were recovered. Problems with the liquid helium supply prevented flights in mid-winter. We have HNO_3 altitude profiles for sunlit summer conditions, spring ozone hole conditions, and late winter conditions.

Our cooled grating spectrometer was flown from Ft. Sumner, New Mexico on 10 October 1994. The payload included a JPL (Dr. Margitan) ozone instrument.

Data were obtained during ascent, along with limb scans before and after sunrise. This flight also studied the horizontal variability in the atmosphere by viewing different directions.

The very high spectral resolution system was flown from Ft. Sumner, New Mexico on 10 October 1995. This flight was very successful, measuring several compounds during sunrise.

Publications

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Far Infrared Measurements of Trace Gases

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Research Objectives

This program is the main component of an International Cooperative Project with Italian and British participation to study atmospheric ozone chemistry. The main program objectives are to provide validation and complementary data correlated with overpass measurements of the Upper Atmosphere Research Satellite (UARS), and to measure the stratospheric concentration of the bromine chemistry sink species, HBr. The effort combines Italian-developed high-resolution Fourier transform spectrometer (FTS) technology, UK-developed sensor system technology, and NASA launch support to achieve high sensitivity for a number of important stratospheric trace species. Our final balloon flight as part of the UARS Correlative Measurements program was made in May 1994. This flight yielded a dataset of outstanding quality, and the retrieval of the HBr altitude mixing profile has been a high priority in our current analysis efforts.

Summary of Progress and Results

Recent concern has focused on the potential threat to the protective ozone layer posed by bromine-containing gases, principally the source gas, methyl bromide. The complex nature of stratospheric chemistry dictates that direct measurements be made in the atmosphere itself as the ultimate check on the modeling of the bromine-related ozone loss chemistry processes. We focused our major effort in the 1994 through 1996 period on improving the measurement sensitivity for HBr by incorporating advanced technology sensors provided to the program by a UK research group. This joint effort has been funded in part by the involved national governments and the Methyl

Bromide Global Coalition industry association. The flight program culminated in a very successful balloon flight from Fort Sumner, New Mexico, in May 1994. This third flight in three successive years completed the planned balloon flight program. In the last year, priority has been given to the analysis for stratospheric HBr, and we have a paper ready for publication which reports the most sensitive measurement obtained to-date of the HBr mixing profile between 20 and 35 km.

Our recent result for the amount of stratospheric HBr agrees with independent measurements by the Smithsonian Astrophysical Observatory group, and serves to reduce one source of uncertainty in the calculation of the bromine ozone depletion potential. Additional analyses remain to be completed using our present datasets for other aspects of the bromine chemistry. The high resolution and quality of the flight data-especially the 1994 flight-is requiring extensive refinements of our analysis algorithms. In addition, some laboratory spectroscopic measurements are needed to refine key line parameters. This supporting spectroscopy effort is conducted with help by the National Institute for Science and Technology and the European Laboratory for Non-linear Spectroscopy. Finally, the results of this program are also contributing directly to the upcoming European-based Airborne Polar Experiment scheduled for deployment in 1997.

Publications

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Far Infrared Balloon Radiometer for OH

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Research Objectives

A stratospheric hydroxyl radical (OH) radiometer is used for balloon observations in the far infrared region of the spectrum. The instrument uses three Fabry-Perot resonators to resolve stratospheric limb emission of OH at 101 cm^{-1} (99 Tm wavelength) and 118 cm^{-1} (85 Tm wavelength). The spectral resolution of 0.002 cm^{-1} is used to match the width of the stratospheric OH emission. The instrument is compact and designed to fly jointly with other balloon measurements. The goal of this task is to determine OH concentrations from 25 to 45 km with better than 10% accuracy. These concentrations are measured as a function of the diurnal cycle and can be used to validate odd hydrogen chemistry in conjunction with other measurements.

An equally compact heterodyne OH instrument is now being developed as a breadboard for the EOS-MLS 2.5 THz OH channel. This new instrument should have 20 times better sensitivity in the 20 to 30 km altitude range.

Summary of Progress and Results

The results from the last five balloon flights have been compared with a simple photochemical model using UARS ozone and water in a paper which has appeared in *Journal of Geophysical Research.* A list of the flights used in this paper is given in Table 1.

Table 1. Recent FILOS Balloon Flights

Date	Place	Other Instruments
2/20/92	Daggett, California	SLS, Ozone
9/29/92	Ft. Sumner, New Mexico	SLS, FIRS, Ozone
5/31/93	Ft. Sumner, New Mexico	IBEX, Ozone
9/25/93	Ft. Sumner, New Mexico	SLS, MkIV, Ozone
5/15/94	Ft. Sumner, New Mexico	IBEX, Ozone

In the last column, *SLS* is the JPL Submillimeter Limb Sounder, *Ozone* is the JPL *in situ* ozone monitor, *FIRS* is the Harvard Smithsonian Astrophysical Observatory Far Infrared Spectrometer, *IBEX* is the Langley/IROE far infrared spectrometer, and *MkIV* is the JPL solar occultation

infrared spectrometer. Both the FIRS and IBEX instruments also measure OH in the far infrared region and data from these flights will allow intercomparison of the three techniques. Generally the FILOS data sets comprise four atmospheric levels averaged over one hour during the middle of the day and half hour averages near sunrise and sunset. The ratios of the observed OH to model OH are given in Table 2.

Table 2. Ratio of Observed OH / Model OH

Pressure	5/94	9/93	5/94	9/92	2/92	Average
21.5	0.55±0.36	0.80±0.57	0.87±0.10	1.36±0.41	1.47±0.39	0.90±0.18
14.7	0.69±0.15	0.95±0.25	0.89±0.11	1.16±0.26	1.64±0.49	0.88±0.17
10.0	0.74±0.12	0.99±0.23	0.78±0.15	1.04±0.24	1.75±0.33	0.87±0.24
4.6	0.82±0.11	0.87±0.19	0.72±0.22	0.93±0.10	1.24±0.16	0.96±0.12
3.2	0.96±0.10	1.02±0.11	0.79±0.29	0.93±0.10	0.97±0.13	0.95±0.08
Column	0.92±0.10	1.04±0.11	0.92±0.37	0.94±0.10	0.94±0.13	0.96±0.05

The row labeled *column* shows the ratios for the integrated column in the range of 25 to 85 km. The other rows show the ratios for the indicated pressure levels.

Since our last flight in May 1994, we have made several hardware improvements in FILOS, which include installation of a rate gyro to improve pointing, installation of higher efficiency power supplies, and removing excess structural weight. The instrumentation effort for FY 1996 has been to prepare for a flight in May 1997 which will compare the Fabry-Perot and heterodyne OH instruments. This new heterodyne instrument is the breadboard test bed for the 2.5 THz OH band on the Microwave Limb Sounder instrument for the Earth Observing System CHEM-1 platform (EOS-MLS), and is being funded by the EOS-MLS project. It is projected to have 20 times more sensitivity for OH than FILOS in the 20 to 30 km altitude range, but will be comparable to FILOS in terms of size. In its first flight, the heterodyne OH instrument will use a liquid helium cooled Nb hot electron superconducting bolometer, which can be replaced with a 65 K high T_c bolometer in later flights. Such a bolometer can be cooled with liquid nitrogen or with a low power mechanical cooler as requirements dictate. The local oscillator is obtained using a photomixer, which generates the LO from the difference of two 850 nm laser diodes. While the costs of development of the heterodyne instrument are paid for by EOS-MLS, the costs of flying the instruments are funded by the Upper Atmospheric Research Program. The benefits of the May 1997 flight are that (1) we will get an early view of the capabilities of the EOS-MLS OH measurement, (2) further measurements of OH by FILOS will be made, and (3) OH from the two instruments can be directly intercompared. We anticipate that the heterodyne instrument would be available in summer 1997 for an arctic campaign, where the enhanced sensitivity for OH at lower altitudes will be particularly valuable.

In the analysis area we have been working with the other JPL teams in an integrated assessment of stratospheric chemistry using the September 1993 balloon flight. We also are working with the IBEX and FIRS teams to intercompare OH observed in the September 1992 and May 1994 flights. The first round of intercomparisons has been made and work is in progress to reconcile the differences. We are also collaborating with the ESA PIRAMYHD team which is studying different instrument approaches for measuring stratospheric OH in the far infrared.

Proposed Work for FY 1997: Reduce data from the Fall 1996 flight, complete OH intercomparison and analysis of the JPL joint balloon flight. Participate in joint balloon flight using the heterodyne instrument in summer of fall 1997.

Publications

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Multisensor Measurements

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Research Objectives

The objective of the Multisensor Measurements task is to provide for continuing technical, logistical, and operational support for stratospheric balloon flights to measure the abundance and altitude distribution of key chemical constituents in the upper atmosphere. Several gondola systems are used which carry single- and multi-instrument packages consisting of *in situ* and remote sensing instruments from JPL and other institutions in the United States and abroad. Data are obtained on the altitude profiles for a number of chemically-coupled species from one or more simultaneous flights in the same airmass which are used for instrument intercomparison purposes and for validation of atmospheric chemical models.

Summary of Progress and Results

In the spring of 1994, two balloon flights were successfully launched from Ft. Sumner, New Mexico. The payload on the first flight on 15 May consisted of Bruno Carli's Infrared Balloon Experiment (IBEX) which was integrated into the balloon program in a cooperative effort between the University of Bologna in Italy and NASA Langley Research Center, and the JPL Far Infrared Limb Observing Spectrometer (FILOS) of Herb Pickett. Four days later, a second flight was launched carrying aloft JPL's MkIV infrared interferometer for Geoff Toon, the Smithsonian Astrophysical Observatory's Far Infrared Spectrometer (FIRS-II) with Wes Traub as the Principal Investigator, and Jim Margitan's JPL OZONE instrument. In the fall of 1994, hardware preparation and logistical support were provided for the OZONE instrument to fly "piggyback" on the Murcray gondola launched by the University of Denver.

The year 1995 was intended by Headquarters to be a year for intensive data analysis and assessment and planning for future campaigns. During this time, the Balloon Support Group did a conceptual design and some detail design for a water-landing composite shell for the MkIV 52-inch gondola. A contract was let during the year for the construction of the shell, which is still in progress. In addition, a conceptual design was put together for a new six-instrument *in situ* gondola; concurrently, four of the six instruments which were to fly on this gondola were themselves being designed and built. The detailed design and fabrication of this gondola and its flight system were begun later that same year.

While there were no flights mounted by the Balloon Support Group in 1995, flight preparation and logistical support were provided for both the Margitan OZONE instrument and the JPL Submillimeter Limb Sounder (SLS) for a Fall flight of the SLS from France and a winter flight for both instruments from Kiruna, Sweden. Both of these flights were successful for the JPL instruments.

In early 1996, the new *in situ* gondola was completed and preparations were made for an engineering test flight with all instruments on board in June from Ft. Sumner, New Mexico. All six instruments were successfully integrated in the field and the flight was launched on June 10. All of the new instruments collected useful engineering data, and the seasoned JPL OZONE instrument and Airborne Infrared Absorption Spectrometer (ALIAS) both returned useful science data. Some RF problems were experienced on this flight between the instruments and the NSBF Command Receiver and this problem is being worked.

At the time of this writing, the MkIV gondola is in Lynn Lake, Canada, awaiting its first northern latitude launch. The Balloon Flight Support Group assisted in the integration, shipping, and field preparations for this flight, then returned to JPL to prepare for continuing operations this fall.

Three more flights are planned for the fall turn-around in Ft. Sumner: a full-up science flight of the new *in situ* gondola with all instruments on board and individual flights of the Pickett FILOS instrument and the Toon MkIV instrument. Current plans call for shipping the *in situ* gondola and instruments to Brazil shortly after the Ft. Sumner campaign for flight operations from that location.

Publications

None

Millimeter and Submillimeterwave Radiometry

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Research Objectives

The objective of this program is measure abundance and variability of stratospheric trace constituents that influence stratospheric ozone using balloon and aircraft-borne millimeter and sub-millimeter wave spectrometers. The present instrumentation uses 3 submillimeterwave mixers at 637 GHz, 604 GHz and 311 GHz to simultaneously measure O_3 and ClO, a key indicator of Cl-catalyzed O_3 destruction, HCl, HO_2, HNO_3, N_2O and H_2O in the stratosphere and upper troposphere. This program also provides a background for development of satellite instrumentation that can yield measurements on a global scale. Technology developed by this program has been used in the Microwave Limb Sounder (MLS) instrument on Upper Atmosphere Research Satellite (UARS) and will be essential to the development of the proposed MLS instrument on the Earth Observing System (EOS) platform.

Summary of Progress and Results

- During 1994-1996, the Submillimeterwave Limb Sounder (SLS) instrument, currently measuring O_3, ClO, HCl, HO_2 near 637 GHz and HNO_3, N_2O near 604 GHz, participated series of five successful balloon flights as part of the Second European Stratospheric Arctic and Mid-latitude Experiment (SESAME) and the UARS Correlative Measurements Program. The goal of these flights was to obtain measurements within the Arctic vortex to better understand the processes controlling the partitioning of chlorine between reactive and reservoir forms and the loss of chlorine-catalyzed loss of O_3. In winter 1994, two flights were performed from the ESRANGE facility near Kiruna, Sweden (68°N). Both flights sampled warm stratospheric conditions showing only slight indication of chlorine activation. In October 1994, an instrument intercomparison and baseline flight was performed from Aire sur l'Adour, France (45°N). In winter 1995, two flights were made from ESRANGE. The first of these flights, on 27 January 1995, sampled air which had been sufficiently cold for heterogeneous conversion of chlorine to occur. This data, shown in Figure 1 (top), indicates complete conversion of chlorine to reactive ClO in regions of the lower stratosphere. The lower panel shows data measured during warm conditions a few weeks later and exhibits a chlorine distribution similar to unperturbed mid-latitude conditions.

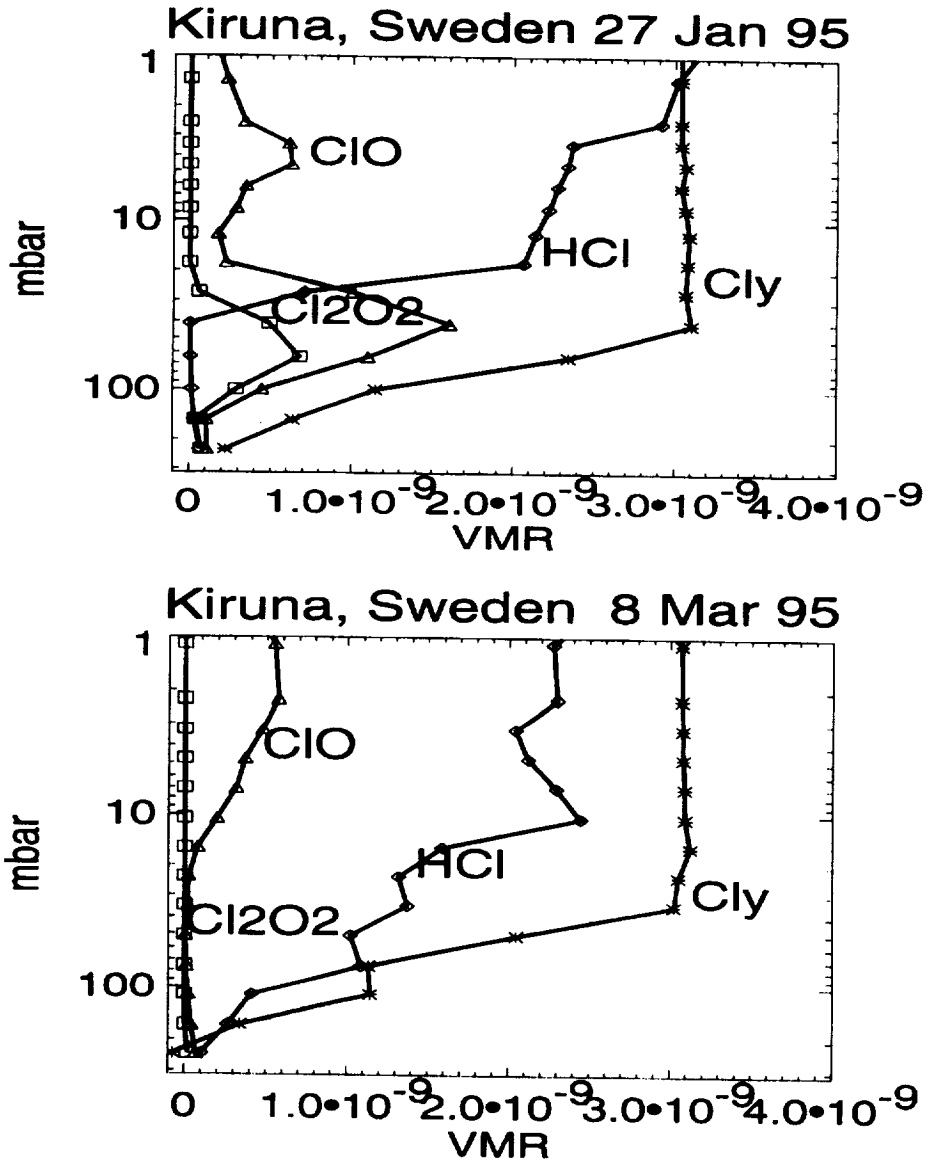

Figure 1. Partitioning of chlorine in the Arctic stratosphere derived from measurements by the balloon-borne submillimeterwave limb sounder over Kiruna, Sweden during SESAME, 1995. (top) Jan 1995 data from within the polar vortex during 'cold' conditions; (bottom) March 1995 data taken outside the vortex during 'warm' conditions.

- A lightweight (50 kg) aircraft version of the SLS instrument has been developed. This instrument, designed for use on the NASA ER-2, will provide continuous vertical profiles for ClO, HCl, O_3, HNO_3, N_2O and H_2O above and below the aircraft altitude.

- Data analysis and publication of results from the UARS Correlative Measurements Program balloon flights is complete. Publications from SESAME 1994-1995 flights are in press and in preparation.

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Stratospheric Fourier Spectrometry

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Research Objectives

This investigation measures the atmospheric abundances of a wide variety of gases which influence atmospheric chemistry or are tracers of transport. These measurements are made by the JPL MkIV Interferometer, a high resolution FTIR (Fourier Transform Infra-Red) spectrometer which operates in the solar absorption mode from the ground, balloons or aircraft. The high resolution (0.01 cm-1) and broad spectral coverage (650 to 5700 cm^{-1}) of the MkIV instrument allow it to measure over 30 different gases simultaneously in the same airmass including CO_2, HCN, CH_4, N_2O, OCS, CHF_2Cl, CF_2Cl_2, $CFCl_3$, CCl_4, $CFCl_2CF_2Cl$, O_3, NO, NO_2, HNO_3, HNO_4, N_2O_5, $ClNO_3$, HOCl, HCl, HF, COF_2, CF_4, SF6, H_2O_2, HCOOH, H_2CO, CO, C_2H_2, C_2H_6, HCN, H_2O and HDO. These observations are then used to evaluate changes and trends, to ground-truth satellite observations, and to test model predictions over the widest possible range of conditions (latitudes, seasons, altitudes, and aerosol loading).

Summary of Progress and Results

Two balloon flight have been undertaken so far during this period; from Ft. Sumner, New Mexico, in May 1994, and from Lynn Lake, Manitoba, in July 1996. Although the latter flight only yielded ascent spectra up to 23 km altitude due to a balloon failure, these will nevertheless be useful in comparing with *in situ* observations made from the ER-2 aircraft which flew over Lynn Lake two days earlier. Further balloon flights are planned from Lynn Lake in August 1996 and Ft. Sumner in September 1996.

Much of our effort has been spent analyzing the spectra from the May 1994 flight, together with those from the three earlier UARS correlative balloon flights performed in 1992 and 1993. The large number of related gases measured simultaneously in the same airmass by the MkIV instrument, allows rigorous testing of models of chemical partitioning and of transport (via tracer-tracer relationships). Examples of MkIV balloon data can be found in the UARS Correlative Measurement Atlas (Peterson and Margitan, 1995). More specifically, the MkIV fluorine budget has been compared with 2-D model predictions and the agreement was found to be excellent [Sen *et al.,* 1995 and Sen *et al.,* 1996a]. However, when Jaeglé *et al.* [1996] examined the chlorine budget they noted a shortfall of total chlorine between 17 and 20 km, which they speculated may be due to heterogeneous chemical reactions forming $HClO_4$. The MkIV balloon profiles have also

been combined with OH measurements from Pickett & Peterson, and ClO and HO_2 profiles from Stachnik, measured simultaneously from the same gondola, to test models of the photochemical partitioning within the HO_x, NO_y and Cl_y families. These data have also been used by Osterman *et al.* [1996] to evaluate production and loss of ozone as a function of altitude. Furthermore, comparison with earlier MkIV balloon flights, performed before the Pinatubo eruption has provided tests of heterogeneous chemistry in the model [Sen *et al.*, 1996b].

We have also been evaluating the MkIV measurement capability in the troposphere, using observations from a September 1993 balloon flight in which high quality sunset spectra were measured all the way down to the surface. Initial results look very promising, although fits to the tropospheric spectra have revealed some serious deficiencies in the current HITRAN molecular spectroscopic compilation (e.g., missing weak bands, inadequate pressure shift and pressure-broadening parameters), even in spectral regions where the stratospheric spectra are fitted well.

We have also made a number of instrumental improvements over the past year: We are anticipating delivery, in the near future, of a water-proof shell which will provide a water landing capability for the MkIV gondola, allowing much greater flexibility in the citing of future field campaigns. The MkIV power supply has been completely rebuilt using new, high efficiency, DC-DC converters. This will not only halve our battery usage, but will also eliminate the need for a radiator plate to dump excess heat, which would otherwise be problematic inside the new waterproof gondola shell. The MkIV suntracker has also been modified to enhance its tracking sensitivity, reduce its mass, and minimize the size of the opening that it needs to look through. These modifications to the MkIV instrument and gondola will reduce the total balloon payload mass to less than 1600 lbs., further improving our deployment flexibility by making it possible to fly on smaller balloons than those used hitherto.

For the past several years we have been making routine ground-based observations in support of the NDSC during the 10-11 months of the year that the MkIV instrument is not involved in balloon or aircraft campaigns. Over the past three years, over 150 days of high quality ground-based observation have been performed from Southern California. These ground-based observations are highly synergistic with the balloon flying: The high sun spectra measured from balloon are used to remove solar and instrumental features from the ground-based spectra, while the ground-based spectra themselves provide a valuable monitor of the health of the MkIV instrument and hence its readiness for future balloon flights.

While JPL is an adequate site for O_3, HNO_3, N_2O, CH_4, CO, HCl and HF measurements, it is too warm and polluted to obtain accurate measurements of NO, NO_2 and $ClNO_3$. For this reason we took the MkIV Interferometer to the Barcroft Laboratory (3.80 km altitude), White Mountain, California, in August 1994 to assess the feasibility of making ground-based observations from there in the future. The site is very dry and sunny and so we proposed in 1995 to the NDSC Steering Committee to make Mt. Barcroft a complementary NDSC site. This was granted in March 1996, however, the implementation had to be delayed one year due to conflicts with proposed balloon flights.

In further support of the NDSC, and we successfully participated in the 1994 ESMOS intercomparison organized by Dr. Rudi Zander in which 17 different investigators performed a blind analysis of a set of 10 ground-based solar absorption spectra. More recently, we also participated in the profile retrieval exercise organized by Dr. Aaron Goldman. In both cases the

MkIV algorithm, which is also used for the analysis of our balloon spectra, performed extremely well. This same algorithm has recently been successfully applied to ATMOS spectra, and forms the basis of a proposal to re-process the entire ATMOS data-set.

We have also collaborated with Dr. Justus Notholt of the Alfred Wegener Institute, Potsdam, Germany. Ground-based spectra from McMurdo (78°S) and Ny-Ålesund (79°N) have been completely re-analyzed using the MkIV analysis software and computer facility. We believe that it is essential to re-analyze different spectral data-sets in a consistent fashion when they are to be compared, otherwise one's conclusions become undermined by any differences in the analysis approaches. Two papers describing this work are close to submission.

Finally, considerable progress has been made over the past 3 years in the ongoing task of archiving MkIV data (spectra and raw interferograms) to CD-ROM. All balloon data are now archived, together with all ground-based data taken during the 1988-1996 period, on a total of 55 CD-ROMs. At the same time that the old interferograms are recovered from tapes, they are completely reprocessed using the current data reduction software, so that the retrieval results will be directly comparable with those obtained recently.

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Measurement of HO_2 and Other Trace Species in the Stratosphere Using a High-Resolution Far-Infrared Spectrometer

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Research Objectives

Our scientific objective is to improve our knowledge of stratospheric chemistry and transport, by making simultaneous measurements of the abundances of about 20 species and isotopes, and interpreting these in terms of current chemical models and transportation processes.

Observations are made continuously, day and night, with a remote-sensing far-infrared Fourier-transform spectrometer (FIRS-2), from a balloon or aircraft, in the far-infrared and mid-infrared spectral regions.

Summary of Progress and Results

We published 20 papers on FIRS-2 results during 1994-96 and are now developing new analytical and experimental tools, as discussed next.

From our 18 flights of the FIRS-2 on board the DC-8, for the 1992 Airborne Arctic Stratospheric Expedition (AASE II), we published 3 papers on chemical change in the Arctic vortex, subsidence of the vortex, and an intercomparison of results from 3 instruments.

Using FIRS-2 data from 9 flights on balloon platforms, including a 1994 flight, we published 5 papers on these topics: a method to estimate ClO from our measurements of HO2, OH, and HOCl, which is important because ClO cannot be measured directly in our current spectra; a detection of HBr and a new upper limit for HOBr, both important for the partitioning of bromine, a strong ozone depleter; a simultaneous measurement of the HO_x, NO_x, and ClO_x families, the first such across-the-board observations in the middle and upper stratosphere; a new determination of $ClONO_2$ in a long wavelength band, confirming previous short wavelength data; and an important paper showing that ozone production and loss do balance in the middle stratosphere, if the additional chemical paths identified in the previous HO_x-NO_x-ClO_x paper are included in the analysis.

With FIRS-2 data obtained on 4 balloon flights for the Upper Atmosphere Research Satellite (UARS) Correlative Investigation Program, we published 6 papers on UARS validation results for the species HNO_3, N_2O, H_2O (2 papers), HCl, and HF, all of which were instrumental in determining the reliability of UARS sensors.

We published 3 papers on data analysis methods for FIRS-2: a database paper containing critical changes in molecular parameters compared to standard compilations; a long paper on data reduction methods unique to our system, including a study of error sources; a paper on a new method of determining linear and non-linear phase variations in Fourier transform spectra.

Another 3 papers were published on instrumentation: an introduction to a special issue of a journal, which we edited; a paper on a new design for beamsplitters which promises to increase dramatically our efficiency and spectral range; and another beamsplitter paper with additional designs.

Recent ongoing work with FIRS-2 data includes: isotope measurements which could help quantify stratosphere-troposphere exchange; extension of our spectral range toward shorter wavelengths, to include new species such as ClO; chemical modeling our past balloon flight data to investigate the issues of photochemical balance and effects of heterogeneous reactions on aerosols; investigations of intrusion of tropical air into mid-latitudes; and preparations for several Alaskan balloon campaigns.

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C. Ground-Based Measurements

Ground Based Monitoring of Water Vapor in the Earth's Middle Atmosphere

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Research Objectives

The goal of this task is to provide the first continuous record of water vapor in the middle atmosphere using ground based radiometers. The instruments are installed at sites of the Network for the Detection of Stratospheric Change (NDSC) and provide the sole source of middle atmospheric water vapor data from these sites. Since water vapor is the primary source of the OH radical and other hydrogen compounds, it is important in controlling ozone chemistry. We are therefore studying the effect of variations in water vapor mixing ratio on ozone. Given the long chemical timescales and rapid variation with altitude of water vapor, we can also use water vapor as a tracer of atmospheric transport.

Summary of Progress and Results

There are now three Water Vapor Millimeter-wave Spectrometer (WVMS) instruments installed at NDSC sites, providing daily measurements of the water vapor profile from 40 to 80 km. All of the instruments have provided nearly continuous data records. The measurements from Table Mountain, California cover the periods January to October 1992, and May 1993 to the present. The data record from Lauder, New Zealand covers the periods from November 1992 to May 1993 and from January 1994 to the present. A third instrument was installed at Mauna Loa, Hawaii, and has been providing data since February 1996. The instruments are all operated remotely from the Naval Research Laboratory, with calibration and emergency support provided by on-site staff.

The WVMS data has undergone a rigorous error analysis, and the 3 instruments have been validated against each other during extensive validation campaigns. The WVMS dataset has been used in the validation of UARS water vapor measurements, and has itself been validated in comparisons with both UARS and ATLAS based instruments. The WVMS validation study shows not only the consistency of individual retrievals, but also the consistency of the seasonal variations observed by the WVMS, HALOE, and MLS instruments. The measurements of the seasonal variation of water vapor in the mesosphere have been shown to be consistent with transport models dominated by advection, but there is also a secondary semiannual cycle which is consistent with the expected seasonal variation resulting from diffusive effects. A study of the effect of seasonal variations in water vapor on ozone is currently underway.

Publications

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Stratospheric and Mesospheric Trace Gas Studies Using Ground-Based mm-Wave Receivers

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Research Objectives

This research deals with field measurements of stratospheric trace gases of importance in the polar or global stratosphere, and is a continuation of the cycle begun in the spring of 1992 with a mm-wave spectrometer of greatly improved sensitivity. We have had two portable mm-wave spectrometers (one older, one improved) in action in Antarctica during the current research period. Both were at McMurdo Station from late August to early October 1994, allowing simultaneous measurements of several stratospheric trace gases during an ozone hole event, and one of these was then moved to the South Pole for an 11-month period of measurements beginning in January 1995. The other spectrometer was again used at McMurdo Station during the spring ozone hole season, from late August until early October 1995. Antarctic field work will be suspended for the austral spring of 1996, due to plans to improve and deploy our equipment at Spitzbergen early in the spring of 1997 for an Arctic intercomparison campaign. New insights have been gained from our research concerning the accuracy of current knowledge about the diurnal chlorine dimer cycle (the primary chlorine cycle destroying lower stratospheric ozone in the Antarctic spring), about the O_3/N_2O ratio over Antarctica and its validity as an indicator of chlorine-induced ozone depletion, about the long-term build-up of active chlorine in the Antarctic stratosphere, about the timing, degree, and altitude range in which nitric acid (HNO_3) is removed from the stratosphere by polar stratospheric cloud formation; about the rate and time span of downward transport in the polar winter stratosphere, and about intrusion of mesospheric air into the polar winter stratosphere. Antarctic field campaigns have been carried out under direct arrangements in the form of nominal or significant grants from the National Science Foundation's Division of Polar Programs, which oversees operations and logistics for all US science carried out on the Antarctic continent; while NASA funding has been vital for all other phases of this research.

Summary of Progress and Results

In the austral spring of 1994, we were able to set up both of our ground-based mm-wave spectrometers at McMurdo to make simultaneous measurements of several stratospheric trace gases during the formation of the 1994 Antarctic ozone hole. One of these, employing an older and less sensitive receiver, had been used in a very successful pioneering experiment to carry out an 11-month cycle of stratospheric trace measurements over the South Pole during 1993. We operated it in tandem with our more sensitive superconducting receiver system. The latter was used to make

difficult chlorine monoxide (ClO) measurements requiring the utmost sensitivity, while the older spectrometer was used for daily measurements of nitrous oxide (N_2O) and nitric acid (HNO_3). N_2O is a useful tracer of vertical transport, and helps distinguish air that has been within the vortex for a considerable period from air which may have recently entered across the vortex boundary. Measurements of strongly depleted HNO_3 are a good indicator of air that has been exposed to very cold temperatures within the vortex, and is chemically primed, via the removal of nitrogen oxides, for catalytic ozone destruction by chlorine. ClO is the intermediary product in the catalytic destruction of ozone by chlorine. This is the first time that vertical profiles for all three species have been measured using ground-based equipment during an ozone hole event. Our results and analysis have been written up and accepted for publication [Klein *et al.*, 1996].

The older spectrometer system was up-dated with new and faster computers, improved operating and analysis software, and minor mechanical improvements, and reshipped to the Pole in January 1995, to follow another annual cycle of trace gas measurements (O_3, N_2O, HNO_3, and NO_2). This time, operations were carried out by cooperative arrangement with Dr. R. Chamberlin, a winter-over astronomer for the Center for Astrophysics in Antarctica. Dr. Chamberlin was simultaneously carrying out a program of tests and observation with a new mm-wave astronomical telescope, and this resulted in fewer measurements, with some longer breaks between, than we had obtained with our own dedicated observer in 1993. Nevertheless, this allowed us to make important comparisons and conformations of the behavior of various trace gases observed during the 1993 cycle (see publications list below). The first in a projected series of papers resulting from the 1995 observations has been written and submitted for publication [Cheng *et al.*, 1996]. The 1995 observations confirm the patterns of trace gas behavior noted in 1993, and give us a good basis for confidence in the rate of downward transport derived for the fall and winter polar stratosphere from NO_2 and O_3 observations; in the timing, degree, altitude range, and severity of HNO_3 condensation into polar stratospheric clouds near the beginning of polar winter; in the generation of new HNO_3 in the middle stratosphere during polar winter; in the timing, duration, and degree of intrusion of mesospheric and thermospheric NO_2 into the middle to upper stratosphere during winter; and the transport of lower latitude air into the center of the vortex at higher altitudes well before it is brought in at lower altitudes.

Our observations of ClO continued at McMurdo during August through October 1995, and the consecutive 4-year record established since 1992 showed an interesting 2-year cycle in the average September amount of ClO, reminiscent of 2-year cycles noted earlier in other Antarctic ozone-depletion parameters, but now harder to trace, presumably due to saturation effects as the hole grew larger. All attempts so far (including ours) to tie strong or weak years of Antarctic ozone depletion to the well known tropical quasi-biennial oscillation cycle have not resulted in any consistent, long-term relation between the easterly or westerly equatorial wind direction and lesser vs. greater ozone depletion, however.

During 1994 through 1995, we developed and applied an in-house photochemical model of the stratosphere, with careful attention to accurate modeling of radiative transfer through the upper atmosphere at large solar zenith angles, to enable us to analyze in detail our own diurnal measurements of polar lower stratospheric ClO during an ozone hole event (essentially the only such measurements existing). This model was the Ph.D. thesis work of D. T. Shindell, who showed that the recommended 1994 JPL photochemical reaction rates for the key reactions governing the ClO dimer cycle are in excellent agreement with observations, and that uncertainty in

some recommended values can indeed be narrowed on the basis of the observed diurnal behavior [Shindell *et al.*, 1995; Shindell and de Zafra, 1996a, b]. V. Chan's Master's thesis developed a very powerful constrained matrix inversion package for retrieval of vertical profiles from multiple lines in one spectrum.

Some improvements are being made to the existing superconducting mm-wave receiver during the latter part of 1996, and we intend to replace the solid-state diode receiver with an ultra-sensitive superconducting receiver in our older spectrometer system before reinstall this system at the South Pole.

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NDSC Ozone Lidar and Instrument Support

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Research Objectives

In earlier stages of this program, the Jet Propulsion Laboratory (JPL) Atmospheric Lidar Team has developed and established laser remote sensing laboratories at the Table Mountain Facility (TMF) in Wrightwood, California, and at the Mauna Loa Observatory (MLO), Hawaii. Both of these sites are stations within the international Network for the Detection of Stratospheric Change (NDSC). The primary and long-term goal is to make regular measurements, 2 to 3 times per week at each site, of the atmospheric profiles of ozone, temperature and aerosols to aid in the detection of changes in the ozone profile and to provide information to assist in the understanding of the reasons for such changes. The results from the TMF and MLO lidars are archived in the NDSC database to add to the global perspective of atmospheric change attained by the network. In the short-term, the results from the ground-based lidars provide correlative and ground-truth measurements for instruments onboard Earth orbiting satellites, such as the Upper Atmosphere Research Satellite (UARS), and onboard research aircraft such as NASA's ER-2 and DC-8. Also in the short-term, we can observe and study the day-to-day variability of these atmospheric parameters.

Summary of Progress and Results

The stratospheric lidars at TMF and MLO are each averaging about 100 measurements per year for each of the parameters measured, i.e., approximately 600 individual profiles per year. The TMF lidar has been operational since February 1988 and the newer lidar was moved to MLO in the summer of 1993 where it commenced routine measurements shortly thereafter. Archiving of ozone and temperature profiles in the NDSC database is up to date with more than 850 sets of profiles from TMF and 350 sets from MLO in the archive.

Recently significant progress has been made in the study of the correlation between aerosol surface density and ozone density using the results from TMF, MLO, and also Ny-Ålesund, obtained since the eruption of Mt. Pinatubo in 1991. The aerosol and tropospheric ozone lidar systems at TMF have been redesigned and separated. These two lidars are making measurements while testing and analysis development continues. An improved analysis for the aerosol lidar measurements at both MLO and TMF is under development. An analysis and intercomparison of the methods and algorithms for the derivation of temperature profiles used by different groups within the NDSC is

being carried out. Ways to improve the analyses applied by JPL and CNRS have been found and the temperature data will be reanalyzed over the next year.

Some modifications were carried out to the MLO lidar to increase the altitude range over which the profiles can be measured. The impetus for these changes was the increased importance in obtaining ozone measurements in the upper troposphere in addition to the stratospheric measurements. To enable these measurements the field-of-view of the telescope was increased so that the laser and telescope would overlap at lower altitudes. These changes were carried out just prior to the MLO3 NDSC intercomparison campaign which was carried out during August 1995. The results from the campaign are still being evaluated and will be published sometime in the near future. The preliminary conclusions for the JPL lidar are that from 20 km to the maximum altitudes reported (i.e., up to 60-km) the JPL lidar results agreed very well with the consensus profile in this region. However, below 20 km the JPL lidar profile showed a positive deviation from the correct profile, increasing as the altitude decreased. This was later determined to be due to a saturation effect caused by increasing the field-of-view of the telescope as discussed above. Following the campaign this problem was thoroughly investigated and a new, different design, photomultiplier tube was installed in all of the receiver channels. The correct operation of the modified system was then verified in several further, informal intercomparisons with the GSFC lidar and the Millitech-NASA LaRC microwave radiometer over the period up to the end of 1995. We are now confident that the ozone results from the JPL lidar are accurate over the range from ~13 km to > 55 km.

Also during 1995 and 1996, the lidar results have been used to support and validate several other NASA programs. These include the UARS Correlative Measurements Program, the STRAT, and TOTE/VOTE aircraft campaigns as they passed through Hawaii, and the SAGE II program.

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Network for the Detection of Stratospheric Change (NDSC) Mobile Lidar

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Research Objectives

Two separate mobile lidar instruments are operated by the Atmospheric Chemistry and Dynamics Branch; a Stratospheric Ozone Lidar, which measures vertical profiles of ozone, temperature and aerosols from the upper troposphere to the upper stratosphere and above; and the Aerosol and Temperature (AT) Lidar which measures vertical profiles of aerosols from the upper troposphere into the stratosphere, and temperature in the upper troposphere to the mesosphere. Both instruments are housed in their own individual trailers, and are independently transportable and self-contained. Within the Network for the Detection of Stratospheric Change (NDSC), Stratospheric Ozone Lidar provides a transfer calibration standard for permanent ground-based ozone lidars, and is used to validate those instruments at the primary NDSC sites.

The AT lidar will perform the same function for aerosols and temperature and provides wavelength dependent data for aerosols. Beyond the NDSC functions, these lidars are used for validation of satellite instruments, participating in both UARS and SAGE II correlative measurement programs.

Summary of Progress and Results

The Ozone Lidar: This transmitter in the ozone lidar was upgraded in the early part of FY 94. A new excimer laser which operates at a 200 Hz pulse rate was installed in place of the older laser which was operating at 50 Hz. This reduced the time required for a complete measurement to 83 min., thereby greatly improving the chances to make a complete measurement. After this modification, the Ozone lidar was shipped to Lauder, New Zealand, a primary NDSC facility, in February 1994, to support the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) campaign, a series of ER-2 flights which deployed from Christchurch, New Zealand. The GSFC Ozone lidar was operated for all four of the ASHOE/MAESA flight periods from March to October 1994. During the four deployments, 80 independent measurements of vertical profiles of ozone, temperature and aerosol backscatter ratio were made on 48 different nights. After the ASHOE/MAESA campaigns, an NDSC intercomparison was held to validate the new Lauder ozone lidar, which was built and operated by Dutch scientists. This was a blind intercomparison, operated under the protocol of the NDSC, and included the lidar instruments, balloon sondes, a millimeter-wave ozone instrument,

and satellite instruments. The results from this intercomparison were presented at the 1995 NDSC Steering Committee meeting.

The lidar was shipped from New Zealand to the Mauna Loa Observatory (MLO) on the island of Hawaii, in May 1995 for another NDSC campaign to validate the newly installed ozone lidar at that site. The lidar was operated from June through August 1995, with the blind intercomparison taking place during the last fifteen days of August. Preliminary data was presented at the 1995 Steering Committee meeting. The lidar remained at the MLO facility through March 1996, and was operated on three different time periods in support of two aircraft missions flown from Barber's Point on the island of Oahu. All data from these missions have been archived in the NDSC Data Archive.

The ozone lidar was returned to GSFC in May 1996, and has been undergoing repairs and maintenance since that time. It will be operated at the GSFC site on clear nights through the end of the year.

The AT Lidar: The AT lidar was tested against the ozone lidar during early 1994. As a result of those tests, some hardware and software changes were made. The instrument made measurements at GSFC for the remainder of the year and in 1995 was shipped to MLO to participate in lengthy field tests and then to participate in the lidar intercomparison which took place in August 1995. Temperature and aerosol comparisons with the GSFC Ozone lidar, the MLO Rayleigh Lidar, and the JPL ozone lidar permanently sited at MLO showed excellent agreement for the GSFC AT lidar. Temperatures retrieved from both wavelengths transmitted by the lidar were self-consistent. Laser problems related to the high altitude of the site (3.4 km) developed in the latter stages of the intercomparison. The trailer was shipped back to GSFC in May 1996 and the lasers have been repaired. Currently a seed laser is being installed into the Nd-YAG laser to provide a narrow spectral output. This will be used to extend our temperature and aerosol measurements downward to near ground level and to provide a better stratospheric temperature measurement during periods of heavy volcanic aerosol loadings.

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Observations and Analysis of Atmospheric Hydroxyl

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Research Objectives

Hydroxyl is a chemically active atmospheric trace species which responds promptly to changes in the photochemistry of the nitrogen and chlorine compounds controlling the abundance of stratospheric ozone, and thus the penetration of solar ultraviolet to the Earth's surface. In the research described here, the vertical column abundance of atmospheric hydroxyl (OH) is determined by measurement of the fractional absorption of sunlight in the P1(1) resonance line of OH at 308 nm. These measurements provide information on the diurnal, seasonal, long term, and geographic behavior of column OH. This behavior is, in turn, a useful diagnostic for constructing and testing atmospheric models used to predict the integrity of stratospheric ozone under changing conditions resulting from anthropogenic emissions.

Summary of Progress and Results

Ground-based OH absorption measurements using high resolution PEPSIOS instruments (Poly Etalon Pressure-Scanned Interferometric Optical Spectrometer) have been made at the following locations:

- Fritz Peak Observatory, Colorado (40°N, 105°W) 1994 through 1996. This is a continuation of the 19-year database initiated in 1977.
- National Institute for Water and Atmosphere, Lauder, New Zealand (45°S, 170°E) 1994 through 1995. This was a continuation of the observations initiated in 1991 using a second instrument of identical design to the Colorado PEPSIOS.
- New Mexico Institute of Mining and Technology, Socorro, New Mexico (34°N, 107°W) April through August 1996. These new measurements have been obtained using the instrument formerly located in New Zealand.

The vertical column OH measurements from all locations since 1980 are highly dependent on solar zenith angle, with maximum at high sun. Recent Colorado data show the persistence of a new seasonal regime which began in 1991. The fall minimum has been consistently depressed about 10 to 15% below the 1980 through 1990 average fall values. While the initial onset of depressed fall abundances occurred a few months after the Pinatubo eruption, there has been no fall OH recovery

correlating with decreased amounts of volcanic aerosol found since spring 1993. The Colorado data also continues to exhibit an AM-PM asymmetry which varies seasonally, approximately in phase with local total ozone.

Comparison of the Colorado database with New Zealand observations has revealed substantial seasonal differences which are well correlated with the breakup of Arctic and Antarctic winter circulations, respectively. The polar vortex breakup in Antarctica occurs about 1.5 months later in season than in the Arctic, and the New Zealand OH perturbation is similarly delayed with respect to Colorado; in both cases the OH perturbation occurs about 6 weeks after the average time of the polar vortex breakup.

Ground-based support for the MAHRSI (Middle Atmosphere High Resolution Spectrograph Investigation) Space Shuttle observations of mesospheric OH in November 1994 was furnished by column OH measurements at Colorado and New Zealand. The column abundances at that time were found to be within measurement uncertainties of earlier average seasonal behavior. The ground-based observations thus indicate the absence of geophysical phenomena which might produce unusually large or small mesospheric OH values.

The New Zealand instrument has been returned to the United States and is currently located at New Mexico Tech, Socorro, NM. Initial comparisons between Colorado (40°N) and New Mexico (34°N) for April through July 1996 indicate small differences in OH column abundances, with New Mexico measurements about 10% above Colorado values for comparable solar zenith angles. Current work at New Mexico Tech involves measurement of P1(1) and Q1(3) absorption by the method of Doppler shift of solar limb spectra. These can be used to infer path weighted temperatures and for validation studies on the standard method of analysis using the single P1(1) line.

Our published steady state calculations for OH have demonstrated that with elevated levels of mid-latitude ClO_x in the lower stratosphere, enhanced HO_x production from the methane oxidation sequence is a possible explanation for the large OH abundances at high sun observed in Colorado since 1980. Attention is currently being given to similar scenarios designed to explain hemispheric differences in OH seasonal and diurnal behavior.

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Ground-Based Infrared Measurements

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Research Objectives

Infrared spectra of the atmosphere contain a wealth of information about the composition and physical state at the time of the observation. Solar absorption spectra can be obtained with very high spectral information, and yields quantitative information for many stratospheric gases. At high latitudes, solar absorption measurements are not possible in the winter, and the spectrum of the thermal emission from the atmosphere is recorded. Our objectives are to obtain infrared spectra from several locations, and to extract the maximum information about the stratosphere and upper troposphere. The derived atmospheric parameters will be studied for evidence of long term change for the Network for Detection of Stratospheric Change (NDSC), for seasonal and other cycles, and will be used for validation of satellite measurements.

Summary of Progress and Results

Our main effort has been to obtain data from Mauna Loa, Hawaii, which is a primary NDSC site. A very high resolution (0.003 wavenumber) solar absorption spectrometer was installed there in 1991, and operated until October 1995. Because this instrument was not completely automatic, spectra were recorded only once a week at sunrise. In August 1995, we installed a fully automatic system (except for liquid nitrogen fills for the detectors). The new system is averaging more than 4 sunrises and 1 sunset per week. During the two month overlap, the column amounts of gases derived from both instruments were compared. The values were generally within 1 or 2%.

Column amounts of ozone have been extensively compared to Dobson observations, with very good agreement. The columns of HCl and HNO_3 have been used for UARS validation. A significant effect on the HNO_3 from heterogeneous chemistry on Mt. Pinatubo aerosols was detected.

We have developed an algorithm for recovering altitude profile information from the infrared spectra for gases with strong enough absorption lines. Ozone profiles derived from Mauna Loa spectra were submitted to the Mauna Loa ozone intercomparison.

Solar absorption spectra have been collected from McMurdo, Antarctic since 1980, in collaboration with New Zealand's National Institute for Water and Atmospheric research (NIWA). The McMurdo instrument has only 0.02 wavenumber resolution, and will be upgraded to 0.003 in December 1996. The higher spectral resolution will allow altitude profiling from McMurdo.

We installed a low resolution atmospheric emission spectrometer system at the South Pole in 1992, and it ran successfully during 1993 as well. In December 1995, a new high spectral resolution (0.1 wavenumber) instrument was installed. Samples of data transmitted electronically indicate that the system is still working well. The higher spectral resolution will permit more accurate HNO_3 measurements during the winter when denitrification occurs, and should allow the measurement of $ClONO_2$. HNO_3 column amounts decrease rapidly in the early winter due to formation of polar stratospheric clouds. The 1993 decrease was significantly later than 1992, even though 1992 had larger amounts of stratospheric aerosols from Mt. Pinatubo. Data from 1996 will provide more information about the denitrification process.

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NDSC Microwave Ozone Instruments

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Research Objectives

The research objectives are as follows:

- To maintain and calibrate the microwave ozone instruments at Mauna Loa, Hawaii, and Lauder, New Zealand to obtain high quality spectral data with minimal interruptions.
- To retrieve ozone mixing ratio profiles over the range 56-0.04 mbar (20 to 70 km) from the spectra.
- To evaluate the quality of the data, and archive all good data in the NDSC database.
- To work with other investigators working at those sites to evaluate the quality of all ozone data being produced at those sites, and attempt to resolve discrepancies
- To assist investigators operating satellite-borne instruments in using our microwave data, as requested.
- To interpret the microwave data scientifically.

Summary of Progress and Results

We have operated a microwave ozone measuring instrument since 1989, first at Table Mountain, California, and later at Lauder, New Zealand. In 1994, we began operating a second, essentially identical instrument, purchased by the Naval Research Laboratory from the Millitech Corporation. Initial operation of the new instrument was at Table Mountain. The original instrument was shipped from Lauder to Table Mountain and intercompared with the new instrument between November 1994 and April 1995. The original instrument was returned to New Zealand and resumed operation at Lauder in April 1995. The new instrument was installed at the Mauna Loa Observatory, its permanent NDSC site, in July 1995.

We participated in two intercomparison campaigns during the 1994 through 1996 period. The original instrument was intercompared with two lidars and a series of balloon-borne ECC

(electrochemical concentration cell) sondes at Lauder in April 1995. The "blind" microwave data (i.e., that submitted before learning results from other investigators) agreed with the Dutch RIVM lidar and the sondes within 7% from 21 to 35 km, and with the GSFC (NASA Goddard Space Flight Center) lidar within 10% up to 42 km. The new instrument was intercompared with GSFC and JPL lidars and sondes at Mauna Loa in July 1995; there, the microwave profiles lay in the middle of the group.

We have published the results of a long term intercomparison study between the original microwave observations at Table Mountain, results from the co-located JPL Table Mountain lidar, and the satellite-borne SAGE-II (Stratospheric Aerosol and Gas Experiment) measurements [Tsou, *et al.*, 1995. These results show that the data from these three instruments are highly correlated on a wide range of time scales. The instruments closely track each other during the seasonal variation of ozone, and show typically 5% or better agreement regarding interannual differences in ozone levels.

Microwave ozone measurements have a unique ability among ground-based remote sensing techniques to measure ozone in the upper stratosphere and mesosphere. We have measured the night to day ratio of the diurnal variation in mesospheric ozone with an uncertainty of 3%. These data have been compared to a photochemical model in Siskind, *et al.* [1995], which has shown that the combination of mixing ratio and night to day ratio profiles can distinguish among different proposed changes in chemical reaction rates.

Our last Table Mountain measurements taken with the original instrument in the spring of 1992 are lower than in the previous two years, by up to 15% for the column density integrated from 25 to 27 km. In 1992, the aerosols from the eruption of Mt. Pinatubo were increasing over Table Mountain. These data are consistent with increased ozone destruction at times of high aerosol loading. However, the 1989 through 1992 Table Mountain record is short, and we are presently adding the new data taken in 1994 through 1995 and using other measurements to evaluate the variability of ozone over the site in the absence of aerosols.

Our microwave ozone data have been used in the validation of all four of the instruments primarily dedicated to stratospheric measurements aboard the Upper Atmosphere Research Satellite. (See the papers by Bailey, *et al.*, Bruhl, *et al.*, Connor, *et al.*, Cunnold, *et al.*, and Ricaud, *et al.* in the special issue of *Journal of Geophysical Research* on UARS validation, Volume 101, No. D6, 1996.) Also, the older Table Mountain record has been used as correlative data for the SBUV/2 (Solar Backscatter Ultraviolet) instrument aboard the NOAA 11 satellite (Planet *et al.*, *Geophysical Research Letters*, *23*, 293-296, 1996).

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Advanced Global Atmospheric Gases Experiment (AGAGE): Coordination, Scientific Analysis, Mace Head and Barbados Stations, and Mass Spectrometers

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Research Objectives

Continuous high frequency gas chromatographic measurements of two biogenic/ anthropogenic gases (CH_4, N_2O) and five anthropogenic gases ($CFCl_3$, CF_2Cl_2, CH_3CCl_3, $CF_2ClCFCl_2$, CCl_4) are carried out at five globally distributed sites (Ireland, California, Barbados, Samoa, Tasmania) in order to determine quantitatively the source and sink strength and circulation of these chemically and radiatively important long-lived gases. Also, *in situ* gas chromatograph-mass spectrometer measurements of a wide range of chlorofluorocarbon replacements and other halocarbons are being made at one site (Ireland) and will shortly begin at a second site (Tasmania).

Summary of Progress and Results

The data for the seven long-lived gases measured in AGAGE during 1994 through 1996 continue to be generally of good quality. Five publications have recently appeared or are about to appear describing and analyzing the data. First, measurements made from 1978 through 1991 of CCl_3F and CCl_2F_2, together with analyses of archived air samples from Cape Grim, showed significantly slowing rates of increase between 1988 and 1991 [Cunnold *et al.*, 1994]. Lifetimes were estimated to be 44 (+17/–10) years for CCl_3F and 180 years (+820/–81) years for CF_2Cl_2. Emission estimates for both gases were consistent with industry data and indicated significant decreases in emissions between 1986 and 1990. Second, global measurements of CH_3CCl_3 between 1978 and 1994 indicate rising concentrations before and declining concentrations after late 1991. The deduced lifetime of CH_3CCl_3 in the total atmosphere is 4.8 (+0.3/–0.3) years, which is substantially lower than previously estimated due largely to a new absolute calibration for this gas [Prinn *et al.*, 1995]. The deduced weighted global average lower atmospheric OH concentration, which measures the lower atmosphere's oxidizing capability, is 9.7 (+0.6/–0.6) radical per cm^3 and this concentration shows negligible trend between 1978 and 1994. Third, observations of CCl_2FCClF_2 between 1982 and 1994, together with analyses of the above 1978–1994 archived air, indicate exponential increases in concentrations up to 1987 and less rapid increases since then [Fraser *et al.*, 1996]. Industry estimates of emissions of this gas exceed those deduced from these observations by about 10% from 1980 to 1993 suggesting that up to 10% of past production may not yet be released to the atmosphere. Fourth, 1987–1994 measurements at Mace Head, Ireland of CCl_3F, CCl_2F_2, CCl_2FCClF_2, CCl_4, CH_3CCl_3, CO_2, CH_4, CO, N_2O, and O_3 have been sorted using two independent methods into two categories: air from the North Atlantic and air from the

European continent [Simmonds *et al.*, 1996]. Concentrations and trends in the two categories differ and use of a transport model enables estimation of the European source strengths of these gases. Fifth, GAGE/AGAGE observations of CCl_3F indicate that its global concentrations reached a maximum in 1993 and decayed slightly in 1994, while CCl_2F_2 concentrations continued to increase, but only slightly in 1993 and 1994 [Cunnold *et al.*, 1996]. These changes imply that world emissions of these gases decreased faster in these two years than industry estimates suggest. Analysis of regional pollution events at Mace Head suggest that industry estimates of the rate of decline in European emissions are too small.

The transition from the GAGE to the AGAGE program was completed in 1996 with all five stations now using the new AGAGE SIO gas chromatographic system. With the 1996 installation of the Finnigan GC-MS system at Cape Grim, Tasmania, we will have one Northern Hemisphere (Mace Head, Ireland) and one Southern Hemisphere station equipped with this moderately high frequency analysis system. The AGAGE instruments and calibrations are described in the companion report from SIO (R. Weiss). See also the companion report for AGAGE: Samoa and West Coast Stations, Calibration, and New Instrumentation, Ray F. Weiss, Scripps Institution of Oceanography (SIO), Principal Investigator.

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Latitudinal Distribution of Tropospheric Concentrations of Selected Halocarbons and Hydrocarbons

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Research Objectives

Measurement of the distribution of selected halocarbons, hydrocarbons, and carbon monoxide is carried out on tropospheric air samples collected at the surface in remote locations over two-week periods every three months, covering the latitudinal range from 71°N to 47°S. Results for CCl_4, CCl_3F, CCl_2F_2, CH_3CCl_3, and CH_4 form part of a continuing set of data from January 1978. Two Halons, $CBrF_3$ and $CBrClF_2$, and methyl bromide (CH_3Br) which were added to our regular analysis in 1991 are the primary tropospheric compounds supporting increasing stratospheric bromine concentrations. Methyl bromide alone represents half of the stratospheric bromine burden, but its atmospheric chemistry is particularly complicated because of its multiple reported sources (oceanic, biomass burning, anthropogenic) and sinks (hydroxyl radical (HO), oceanic, soil), about which relatively little quantitative data are available. Numerous non-methane hydrocarbons (NMHCs) are measured in this study. The latitudinal distribution and temporal trends in the concentrations of these and other short -lived gases quantified in this study provide constraints for computer models and allow for estimating emission strengths and removal processes.

Summary of Progress and Results

The entirely anthropogenic gas, perchloroethene (C_2Cl_4), has a strong gradient of decreasing concentrations from the Northern to Southern Hemisphere, with very low concentrations in the Southern Hemisphere throughout the year, consistent with its predominant input from the Northern Hemisphere. The late-winter maximum and late-summer minimum in the Northern Hemisphere are strongly coupled to the atmospheric abundance of HO, the only important species responsible for C_2Cl_4 removal. Using our measurements of the global atmospheric burden along with estimates of its emissions, the lifetime of C_2Cl_4 was calculated to be about 5.4 months. This is in good agreement with the 4.0 month estimate obtained by comparison of C_2Cl_4 and CH_3CCl_3 reaction rate constants, assuming an atmospheric lifetime for CH_3CCl_3 of 5.7 years. The fact that these two methods agree well suggests current global average HO concentrations obtained from the CH_3CCl_3 lifetime calculations are reasonably accurate.

Emissions of the three primary chlorofluorocarbons have slowed markedly during the 1990s in response to the regulatory restrictions of the Montreal Protocol. September 1995 ambient levels of CFC-11 and CFC-113 were decreasing. Although yearly emissions of CFC-12 estimated from

our measurements have decreased by more than 60% from 1988 to 1995, the remaining emissions were still large enough to sustain a growth rate of about 4 pptv/year at the end of 1995.

Since 1990, there has been considerable short-term variation in the CH_4 growth rate, particularly in the Northern Hemisphere. The global growth rate for late 1994/early 1995 was approximately 5 ppbv/year but with indications of further oscillations. The reason for these short and long-term changes have not been conclusively identified but changing natural gas emissions/leakage have been reported as a partial cause.

Our latitudinal and seasonal NMHC data furnish unique information which provides an excellent record of the effects from seasonal fluctuations in HO concentrations. When combined with the vertical NMHC distributions measured during the various NASA and NSF aircraft field missions that we have taken part in since 1988, we can estimate the atmospheric burden of these gases. For example, average annual burdens have been calculated to be 640 ± 60 pptv for ethane; 120 ± 30 pptv for ethyne; and 100 ± 30 pptv for propane over the period March 1994 through March 1995. This information allows source strengths and source latitudinal distributions to be derived, which in turn can provide useful information about sources such as biomass burning, which has a significant Southern Hemisphere component. Preliminary global flux estimates are 15 Tg/year for ethane; 9 Tg/year for ethyne; and 17 Tg/year for propane. Our quantitative measurements of a comprehensive range of hydrocarbons have been validated by our successful participation in a series of NSF sponsored NMHC intercomparisons.

Methyl bromide, with a remote atmospheric mixing ratio between 9 to 12 pptv, accounts for about half of the total carbon-bonded bromine in the troposphere. Although these concentrations are quite low, brominated radicals react very quickly with chlorine monoxide (ClO) and hydroperoxy radicals (HO_2), contributing significantly to stratospheric ozone loss. The quantitative evaluation of CH_3Br is particularly complicated, because of its reported multiple sources (oceanic, biomass burning, anthropogenic) and sinks (HO, oceanic, soil), but is important for calculation of its ozone depletion potential (ODP). From 6 air sample collections, it was observed that the seasonal concentration of CH_3Br in Alaska varied sinusoidally with an R^2 value of 0.95, an amplitude of 1.3 pptv, and a phase consistent with HO removal. The absence of any pronounced seasonal variation of CH_3Br concentrations in New Zealand implies the Southern Hemisphere must have one or more seasonal influences in opposition to HO removal. The curve has a maximum at about 1.34±0.05 in March and the minimum at 1.07±0.05 in September.

Publications

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UV/Visible Interferometery

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Research Objectives

A new high resolution ultraviolet-visible Michelson interferometer, called the FTUVS, is recording solar and zenith sky spectra in the 300-450 nm spectral region for ground-based studies of stratospheric trace gas composition. The instrument is located at JPL's Table Mountain Facility near Wrightwood, California. The FTUVS measures the diurnal column density of the OH radical by differential Doppler solar absorption spectroscopy. The column densities of several other important atmospheric species including O_3, NO_2, NO_3 and BrO will be measured by zenith sky and direct solar spectroscopy. In collaboration with Professor Yuk Yung at Caltech and his students under joint National Science Foundation funding, the data will be used in studies of the stratospheric HO_x and NO_x budgets. The feasibility of using this instrument for measurement of long-term trends as part of the Network for the Detection of Stratospheric Change (NDSC) will be assessed.

Summary of Progress and Results

Work continued this FY on the development of the FTUVS at Table Mountain Facility for use in high resolution solar measurements of the OH column abundance. The work this year was highly successful. In May 1996, the first OH spectra were obtained with the FTUVS instrument. Six strong and two weaker absorption lines were identified in ratio spectra of the east and west solar limbs. The signal-to-noise ratios of the spectra were good, and the resulting spectra were about the same quality as spectra obtained by the premier solar interferometer at Kitt Peak. Procedures are currently being developed to retrieve the OH column abundance from the observed spectra in collaboration with Professor Yuk Yung at Caltech.

Progress was also made in the area of ozone remote sensing. A new method was developed to detect the tropospheric ozone change at ground based stations using measurements of direct and diffuse solar radiation in the Huggins bands from 310 nm to 345 nm. Due to larger multiple scattering effects in the troposphere compared to that in the stratosphere, the optical path of tropospheric ozone is markedly enhanced (as compared with the stratospheric ozone). Preliminary measurements of the scattered sky radiation are being made with the FTUVS to assess the validity of the radiative transfer calculations.

Publications

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Ground-Based Measurements of Stratospheric ClO as Part of the NDSC — SUNY, Stony Brook

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Installations: Mauna Kea, Hawaii and Scott Base (near McMurdo), Antarctica

Research Objectives

Chlorine oxide, ClO, is the principal chemical involved in the catalytic destruction of ozone by chlorine from CFCs and other man-made chemicals.

The objective of this research is to measure the content and distribution of ClO from ground-based stations using the technique of millimeter-wave spectroscopy. This is the same technique we previously employed to make the first measurements of a huge excess of ClO in Antarctica during the National Ozone Expedition in 1986. This work is in close collaboration with Alan Parrish of Millitech Corporation who built the instruments. The goals for this project are:

- To monitor the ClO content of the atmosphere on a long-term basis using our instruments at Mauna Kea, Hawaii and Scott Base, Antarctica as part of the Network for the Detection of Stratospheric Change (NDSC). Data acquisition is monitored and controlled from SUNY at Stony Brook. The data are downloaded daily to Stony Brook where they are stored and processed.
- To obtain altitude profiles of ClO from 16 to 47 km to be used as part of the complete picture of the stratosphere.
- Comparison of ground-based with space-based measurements of ClO. The latter include measurements made by Upper Atmosphere Research Satellite (UARS) and any future space-based missions. These ground-based instruments will also be the major source of complete altitude profiles of ClO if space-based instruments cease operations.
- Intercomparisons of the three millimeter-wave ClO instruments built by Millitech to check for consistent calibration. Two of these have already been compared in Hawaii with excellent results. The French instrument has been brought to Hawaii (July 1996) for intercomparison.

Summary of Progress and Results

Status of Instruments

On January 1992, one of the new ClO instruments (A) built by Millitech was installed at the Stony Brook site on Mauna Kea, Hawaii (latitude 20°N, altitude 4060 m). The instrument operates automatically under computer control 24 hours a day. A second identical instrument (B) was installed on October 1993 and both instruments were operated simultaneously from October 1993 to July 1995. A continuous record of ClO altitude profiles was obtained from October 1993 until July 1996. About 30% of the time the weather is extremely good and data taken under these conditions provides the primary database.

We have started a collaboration with the New Zealand Antarctic program to carry out our ClO Antarctic measurements. Instrument B was shipped to New Zealand on December 1995 for transfer to Scott Base, Antarctica (latitude 78°S). Data acquisition can be monitored and controlled from SUNY at Stony Brook as is the case with the instrument in Hawaii. This instrument is providing the first all year record of the ClO altitude profile from Antarctica, a critical database for monitoring the Antarctic Ozone hole.

Mauna Kea, Hawaii Site

The arrangement between Stony Brook (P. Solomon) and the Caltech Submillimeter Observatory for the maintenance of the instruments and the building is working well. A technician is employed part time by Stony Brook through an arrangement with Caltech to check on the NDSC instruments. We have been engaged in extensive tests of the instrumental calibration of both instruments and the results have been excellent. For the period of October 1993 to July 1996 we have approximately 75 weeks of good quality data obtained at Hawaii. This dataset is the only continuous set of observations of ClO at middle latitudes from the ground. Together with our data from our previous instruments (from 1982 onward), we have available ground-based observations of ClO which can be used to study long term trends.

After reducing and analyzing the data for this period, October 1993 to July 1995, we have deposited the data in the NDSC archives to be available to the greater scientific community for research and analysis. The major scientific results are:

- There has been a 40% increase in middle (30 to 45 km) stratospheric ClO from the period 1983 to 1995. This is in good agreement with that expected from models of the production of CFCs and transfer into the stratosphere.
- There is a good correlation between our low altitude ClO and the presence of Mt. Pinatubo aerosols. This demonstrates the operation of heterogeneous chemistry in the Pinatubo aerosol cloud. The ClO in the lower stratosphere (20 to 27) km is higher in 1992 than late 1993-1994 and 1994 is slightly higher than 1995. The Mt. Pinatubo particles were gone by January 1995 but were still present in the first 6 months of 1994, although reduced by a factor of 2 or 3 from late 1992.
- The middle stratospheric ClO altitude profile is in good agreement with models.
- There is good agreement with UARS latitude averaged profiles to within the errors. The UARS mid-stratospheric profiles have larger errors.

Scott Base, (McMurdo) Antarctica

The instrument was shipped to Antarctica in mid-January 1996 and it was installed and tested successfully by mid-February 1996. Data from March to 1 August 1996 show the presence of middle stratospheric ClO with a day - night variation as expected. We are currently awaiting data from the beginning of the 1996 Antarctic ozone hole.

Publications

A manuscript summarizing the Mauna Kea results is in preparation. A thesis by Q. Chen titled "Retrieval Techniques for Ground Based Millimeter measurements of Stratospheric Constituents" was completed in 1995.

Advanced Global Atmospheric Gases Experiment (AGAGE): Samoa and West Coast Stations, Calibration, and New Instrumentation

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See also the companion report for AGAGE: Coordination, Scientific Analysis, Mace Head and Barbados Stations, and Mass Spectrometers, Ronald G. Prinn, Massachusetts Institute of Technology (MIT), Principal Investigator.

Research Objectives

Continuous high frequency gas chromatographic measurements of two biogenic/ anthropogenic gases (CH_4, N_2O) and five anthropogenic gases ($CFCl_2$, CF_2Cl_2, CH_3CCl_3, $CF_2ClCFCl_2$, CCl_4) are carried out at five globally distributed sites (Ireland, California, Barbados, Samoa, Tasmania) in order to determine quantitatively the source and sink strength and circulation of these chemically and radiatively important long-lived gases. Also, *in situ* gas chromatograph-mass spectrometer measurements of a wide range of chlorofluorocarbon replacements and other halocarbons are being made at one site (Ireland) and will shortly begin at a second site (Tasmania).

Summary of Progress and Results

The major objectives of the SIO contribution to AGAGE have been the development and implementation of new instrumentation for the measurement of the above compounds at all of the AGAGE field sites and at the calibration laboratory at SIO, the upgrading of all the field sites with this instrumentation, the development of new primary calibration standards for these compounds, and the implementation of a network of accurate secondary standards to calibrate the field measurements. All of these goals have now been achieved, and the AGAGE program has fully replaced its GAGE predecessor.

The new instrument system for AGAGE incorporates many significant technological advances. The system is based on a custom-designed automatic gas sampling and flow control system, to which are fitted a Hewlett-Packard 5890 gas chromatograph with two electron capture detectors and a Carle gas chromatograph with a single flame ionization detector. All operations and data acquisition are by a Sun Microsystems workstation computer using: custom runfile architecture, custom signal processing and integration routines, and digital storage of all the data and chromatograms. The instrument measures its own non-linearity for all the AGAGE gases on a regular basis using a pressure-programmed constant-volume injection system and a single gas standard. All channels of the instrument are fitted with precolumns to avoid column contamination by late-eluting gases, and as a result the frequency of measurement has been increased three-fold

versus GAGE. Precision is also greatly improved over the GAGE instruments. The system works interactively with its uninterruptible power supply so that controlled shutdown and startup of the entire instrument and sampling system are assured when there are extended power outages. Installation of these instruments in the field has included the design, fabrication and installation of new custom laboratories at the Trinidad Head, California, and Ragged Point, Barbados, sites. With the instrument installation at Samoa completed in August 1996, the new AGAGE instruments are now operational at all five AGAGE stations.

The development of new absolute calibration scales has been accomplished using an extension of the ``bootstrap'' calibration method used earlier at SIO. In the AGAGE work, gravimetrically determined aliquots of pure CFCs are mixed with about 12 liters of gravimetrically determined pure nitrous oxide. A small aliquot (~0.4 cm^3) of this mixture is then introduced into a 35 liter electropolished stainless steel canister to which about 10 torr of water vapor has been added to reduce wall reactions and adsorption. The canister is then filled with about 40 atmospheres of re-purified ``zero air'' to bring the nitrous oxide mole fraction to a near-ambient value. The resulting nitrous oxide concentration is then calibrated gas chromatographically against existing SIO standards, and the CFC concentrations are determined by multiplying the measured nitrous oxide mole fraction by the gravimetric CFC/nitrous oxide ratios of the original mixture. In this way we have been able to obtain improved accuracy for all AGAGE gases, but especially for the lower vapor pressure and more adsorptive gases. We are now extending these calibration methods to other compounds of environmental interest, including selected HCFCs, other hydrohalocarbons, and methyl halides. These extensions in our primary calibrations are also being applied to the new AGAGE GC-MS installations. We are also engaged in international intercalibration exercises (through the IGAC/NOHALICE Activity) for all the AGAGE gases as well as for methyl halides and some HCFCs. Finally, we have devoted considerable effort to develop reliable and clean methods to compress and store background ambient air for use as secondary standards at the stations and for archival purposes. The AGAGE network is now calibrated using secondary standards prepared and calibrated at SIO, and work on further improvements in storage containers in continuing.

The improvements in AGAGE analytical capabilities summarized above provide the experimental foundation of the AGAGE scientific results summarized in the companion AGAGE report from MIT (R. G. Prinn, Principal Investigator).

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D. Aircraft-Borne Measurements

Southern Hemisphere *In Situ* Observations of OH, HO_2, ClO and BrO from the ER-2 Aircraft for the 1994 ASHOE Mission

Principal Investigator: James G. Anderson

Co-Investigators: Paul O. Wennberg, Thomas F. Hanisco, Richard M. Stimpfle, Daniel W. Kohn, Ronald C. Cohen, Elliot M. Weinstock, and Eric J. Hintsa

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Research Objectives

The Airborne Southern Hemisphere Ozone Experiment (ASHOE) was organized to address the following issues:

- The downward trend in total ozone at sub-polar and mid-latitudes is large and has been observed year-round, with the greatest trends occurring when the vortex is cold enough to support the formation of polar stratospheric clouds, that initiate the chlorine based chemistry that causes the Antarctic ozone "holes."
- The spreading of the ozone "hole" to mid-latitudes.
- The relationship between ozone loss in the very lowest part of the stratosphere and the greenhouse effect.
- The role of aerosols in perturbing lower stratospheric chemistry.
- The transport of material injected into the lower stratosphere at tropical and mid-latitudes is a central issue in assessing the effects on stratospheric ozone by exhaust emissions from possible future high-speed civil transport aircraft.

This research effort focused on the simultaneous observation from the NASA ER-2 aircraft of the radicals listed in the title.

Summary of Progress and Results

In situ observations of the BrO radical in the lower stratosphere from the Arctic boundary to the Antarctic obtained simultaneously with measurements of hydrogen, nitrogen and chlorine radicals, establish that bromine radicals occupy the rate limiting step in catalytic cycles that constitute more than half the halogen destruction rate of ozone over the region sampled. The latitude dependence of each of the catalytic cycles rate limited by bromine is shown in Figure 1.

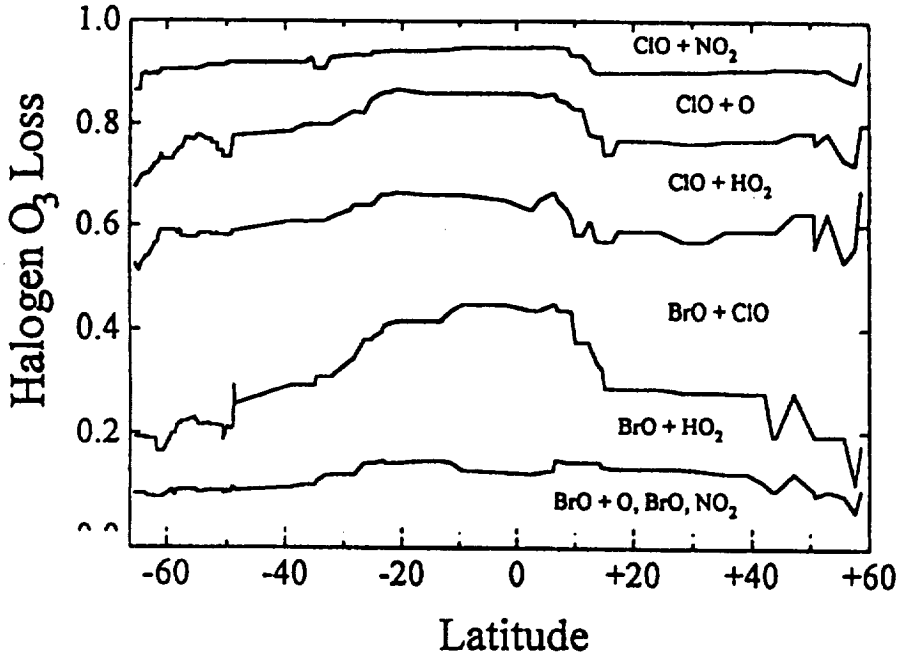

Figure 1. The observed fractional contribution of the halogen catalyzed ozone loss cycles, identified by their rate-limiting steps *versus* latitude.

These observations demonstrated that bromine is 60 to 80 times more efficient per atom than chlorine. Inferred total stratospheric inorganic bromine agrees within error with tropospheric measurements of organic bromine compounds that enter the stratosphere from below. A key conclusion emerging from these observations is that predicted halogen induced ozone destruction must include secular trends in bromine.

In flights out of Christchurch, New Zealand, by the ER-2, the opportunity arose to sample the exhaust plume of the Air France Concorde. The interception was successful, yielding simultaneous, *in situ* observations of CO_2, H_2O, NO_y, OH, and HO_2. Gas-phase reactions with OH, long thought to be the rate-limiting step in the production of aerosols in aircraft exhaust, are investigated with *in situ* measurements of HO_x, (OH and HO_2) in the exhaust plumes of an Air France Concorde and a NASA ER-2 in the lower stratosphere. Enhanced concentrations of OH result from the photolysis of HONO, which is formed in the early stages of the exhaust. Reactions of OH with O_x control the lifetime of HONO and hence oxidation of all species by OH in the plume. The measurements of OH imply that gas-phase reactions of this radical oxidize only a small fraction of NO_x (5%) and SO_2 (2%) in the exhaust of the Air France Concorde, indicating that oxidation of OH in the plume is not responsible for generating the large number of particles observed in the exhaust wake of the Concorde.

Simultaneous, *in situ* measurements of the radicals OH, HO_2, and ClO, made from the NASA ER-2 aircraft during the flight of 30 July 1994 of the ASHOE/MAESA field campaign, are used to test the effect of heterogeneous production and loss of HOCl on the concentrations of

HO_x (HO_2 + OH) in the Antarctic vortex. The data are consistent with a net loss of HOCl occurring on liquid sulfate aerosols at temperatures below 194 K and with a net production of HOCl on the aerosols at temperatures between 196 to 200 K. A model that does not include loss of HOCl by the liquid sulfate reaction HOCl + HCl overpredicts the HO_x data by an order of magnitude at temperatures below 194 K. Between 196 to 200 K, the HO_x data differ by 30% from a model including gas-phase only photochemical production and loss of HOCl and by 30% from a model that does not allow the gas-phase release of HOCl produced by heterogeneous reaction of $ClONO_2$ + H_2O. At all temperatures below 200 K, the best agreement with the data is obtained with a model that includes the heterogeneous chemistry of HOCl at the known laboratory rates.

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High-Altitude Aircraft and Balloon-Borne Observations of OH, HO_2, Cl, ClO, ClOOCl, O_3, $O(^3P)$ in Earth's Stratosphere

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Co-Investigators: Paul O. Wennberg, Thomas F. Hanisco, Richard M. Stimpfle, Daniel W. Kohn, Ronald C. Cohen, Elliot M. Weinstock, and Eric J. Hintsa

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Research Objectives

The global distribution of ozone in the stratosphere depends on the balance between production, loss, and transport. The research carried out under this grant addresses those processes that control the destruction rate of ozone—the analysis of the rate-limiting radicals that control the catalytic loss rate of ozone in the stratosphere. Four questions establish the objectives of the research: Why is ozone thinning over mid-latitudes of the Northern Hemisphere? How, in the future, will the global distribution of ozone change in response to changes in chlorine, bromine, hydrogen, and reactive nitrogen concentrations in the stratosphere, and to changes in aerosol loading of the stratosphere? Under what conditions will the Arctic vortex region emulate the dramatic loss of ozone within the Antarctic winter vortex? Will the proposed High Speed Civil Transport harm stratospheric ozone?

This research requires a combination of instrument development, laboratory studies of instrument performance and calibration, field deployment of those instruments on the NASA ER-2 aircraft and the analysis and publication of data obtained on those missions.

Summary of Progress and Results

A central objective of the research is to map the absolute concentration of the rate limiting free radicals as a function of altitude, latitude, season, aerosol loading over the domain reachable by the ER-2. Simultaneous *in situ* measurements of the concentrations of OH, HO_2, ClO, BrO, NO, and NO_2 extending from the southern fringe of the arctic circle to the Antarctic demonstrate that the radical catalyzed rate of ozone destruction is dominated by hydrogen and halogen species, specifically HO_2, ClO, and BrO. Catalytic destruction of ozone by NO_x, rate limited by NO_2, which for two decades was believed to dominate ozone destruction rates, accounts for less than 20% of the total ozone loss rate. Figure 1 displays a sample of the vertical distribution of the

hydrogen, halogen and nitrogen rate-limiting steps as a function of latitude in the Northern Hemisphere.

The key conclusion from this discovery is that the response of the ozone concentration in the lower stratosphere to increasing concentrations of NO_x, *reverses* in sign with respect to our previous understanding—specifically, the loss rate of ozone decreases with increasing NO_x loading. This is particularly critical for analyses of the impact of the proposed High Speed Civil Transport. In the *lower* stratosphere, the release of NO_x by the aircraft will decrease the rate of ozone catalytic loss rather than increase the rate as would be the case for a nitrogen radical controlled system. This behavior is captured in Figure 1.

The inversion in sign is a reflection of the coupling reactions between the key rate limiting radicals. These coupling reactions dictate the *response functions* of the stratosphere to changes in the concentration of reactive nitrogen, hydrogen, chlorine bromine, aerosol loading, etc.—the derivative of a given rate-limiting radical concentration to a specific change in one of those variables. A key development in this research is the ability to directly observe these derivatives, these *response functions.* A key example is shown in Figure 2, displaying the partial derivative of the rate-limiting ClO radical concentration with respect to No_x.

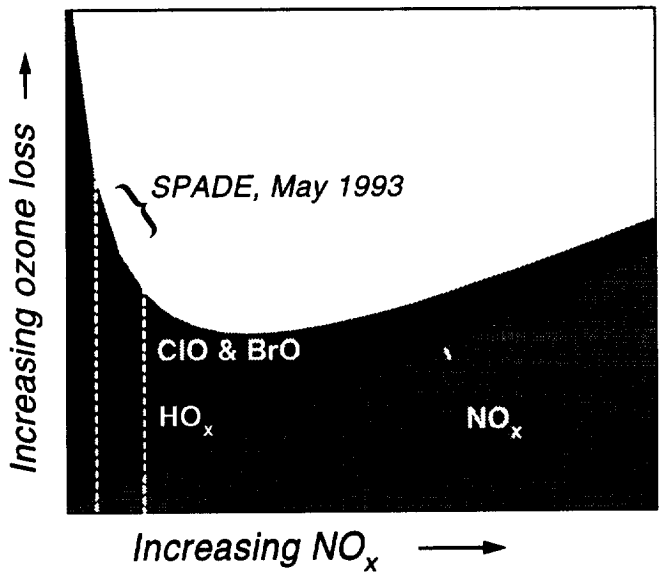

Figure 1. The O_3 removal rate is shown versus [NO_x]. Because of the coupling that exists between the radical families, the response of the total O_3 removal rate to changes in [NO_x] is highly nonlinear. At sufficiently low [NO_x], such as observed during the SPADE campaign, the removal rates are inversely correlated with [NO_x].

A key conclusion emerges from this analysis. The dominance of hydrogen and halogen radicals in the destruction of ozone, a result of the key role played by aerosols in the conversion of NO_x to nitric acid, in combination with the fast coupling reactions that link the hydrogen and nitrogen

systems and the chlorine and nitrogen systems, places the region of maximum risk in the low NO_x domain. Thus in a global sense, the major opportunity for misjudgment in calculated (modeled) ozone loss, lies in the low NO_x condition. Given this rearrangement in our understanding of the lower stratosphere and observations of the Concorde wake and of the ER-2 wake that includes simultaneous observations of CO_2, H_2O, NO_y, OH, HO_2, ClO and particles, attention has turned to an analysis of how the aerosols generated by the proposed HSCT will alter (reduce) the NO_x loading of the lower stratosphere.

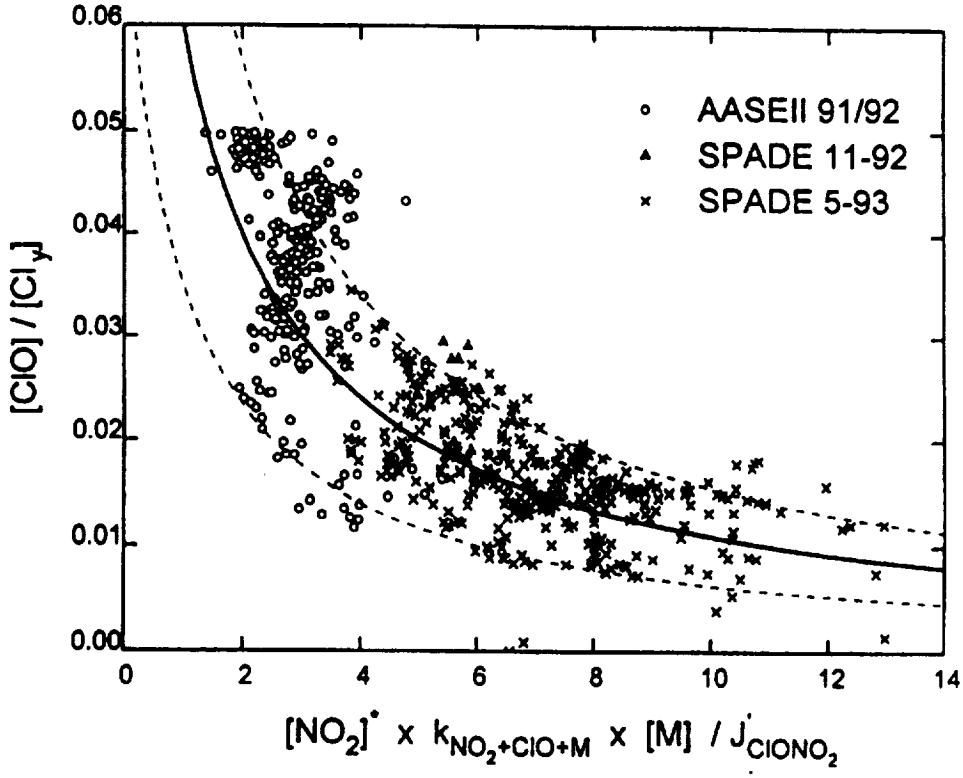

Figure 2. The observed ratio of $[ClO]/[Cl_y]$ versus $[NO_2]^*$.

Analysis of the BrO data extending from the arctic circle to the Antarctic demonstrates that (1) greater than half of the halogen catalyzed destruction rate of ozone involves bromine in the rate determining step; (2) on a per-atom basis, bromine is 60 to 80 times as effective as chlorine in the destruction of ozone; and (3) the radical-inorganic reservoir in the lower stratosphere is quantitatively consistent with the organic source in the troposphere.

A key species linking the nitrogen and chlorine reaction network that also constitutes a major fraction of the inorganic chlorine reservoir, specifically chlorine nitrate, has been a key missing constituent in the ER-2 measurement arsenal. The development of a new instrument to detect $ClONO_2$ as well as NO_2, ClO and BrO has been designed and built for the ER-2. That instrument flew for the first time in July 1996.

A key component of stratospheric ozone research centers of processes that control the transport of constituents in the stratosphere and the exchange of species between the stratosphere and troposphere. *In situ* observations of ozone and water vapor from the ER-2 supported by this grant investigated the seasonal cycle of water vapor in the tropics demonstrating that the hygropause is not caused by deep convection of dry air but rather is a manifestation of temperature driven seasonal cycles superposed on vertical motion. Key simultaneous observations were made of CO_2 and water vapor using the Harvard fast response H_2O instrument.

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Trace-Gas Measurements for Whole-Air Sampling

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Research Objectives

Our research objectives for 1994-1996 were: 1) refine our calibrations of various organic halogens; 2) continue data analysis from AASE II; 3) test the feasibility of using the Whole Air Sampler (WAS) during the Stratospheric Tracers of Atmospheric Transport (STRAT) missions to provide data on short-lived (weeks to months) trace gases; 4) modify the Whole Air Sampler for deployment in the left superpod nose, and in the right superpod mid-body for the 1996 STRAT missions; 5) characterize distributions of short-lived halocarbons and hydrocarbons in the upper troposphere/lower stratosphere tropics and mid-latitudes; 6) evaluate transport rates calculated from halocarbon distributions; and 7) characterize and quantify the speciation of organic bromine in the upper troposphere/lower stratosphere.

Summary of Progress and Results

Our laboratory work involved assessments and refinements of calibrations for compounds previously measured in whole air samples as well as for the short-lived trace gases measured during the STRAT campaign. Calibration of all species is an ongoing process that involves standard preparations using both static and flow dilution systems. We also participated in successful intercalibrations for several halocarbons with the NOAA Climate Monitoring and Diagnostics Laboratory (including intercomparisons with the ACATS instrument). For the STRAT flights we used the following instrumentation: a GC/MSD (also used on earlier NASA missions); a newly developed GC/NICI/MS (for high sensitivity analysis of bromo- and iodocarbons); a redesigned GC/FID instrument (for high sensitivity C2-C5 NMHC analysis), and a second GC/FID instrument for methane analysis.

Our data analysis involved both tropospheric and stratospheric datasets. We reported a strong latitudinal gradient of HCFC 141b mixing ratios in the marine boundary layer from samples collected during a cruise in the Pacific. The data from the cruise, together with data collected during AASE II, allowed us to calculate global emissions of HCFC 141b for 1990-1993 using a box model. We also found a north/south latitudinal gradient of 1.3 in CH_3Br mixing ratios from a composite of cruise data. We evaluated the age of stratospheric air, relative to the time of entry from the troposphere, using CFC 115 and CO_2 mixing ratios from AASE II. Calculations using both species gave similar results. Between 325 K and 500 K air outside the polar vortex was

between 1 and 4 years old while air inside the vortex was between 4 and 6 years old. The deduced ages were used with concurrent measurements of organic chlorine and bromine containing halocarbons to determine inorganic chlorine and bromine as a function of latitude and altitude. Inferred Cl_y and Br_y abundances generally increased with increasing latitude and altitude. For our analyzed locations inside the polar vortex, we estimated a maximum Cl_y abundance of about 2.7 ppbv and a maximum Bry abundance of about 13.7 pptv. The locations of these maxima corresponded to an average N_2O mixing ratio of about 100 ppbv and to a fractional dissociation of organic chlorine and bromine of 0.85 and 0.90, respectively.

In addition to our data analysis and lab work, we have suggested a physical mechanism that may influence the trends of trace gases. Specifically, we show that if heating from volcanic aerosols were of sufficient magnitude to significantly increase stratospheric circulation, the response in the troposphere would be a decline in the increasing trends of N_2O and CH_4. The decline results from a higher degree of exchange between the troposphere and stratosphere, which contains lower mixing ratios of both gases.

During STRAT test flights in March and May 1995, the WAS collected replicate samples during vertical descents of the ER-2. Fourteen pairs of samples were collected during each test flight in March and May. The purpose of this test was to document the reproducibility of whole air collection in stainless steel containers, and to assess the analytical precision of different analytical instruments used for compound quantification. In addition to these profiles, a set of three samples was collected in the mid-troposphere during one flight. This flight provided an excellent contrast to those in the lower stratosphere, and indicated the potential range of trace gas mixing ratios accessible for studying mixing processes in the upper troposphere/lower stratosphere. A full range of analytical procedures were applied to the samples to determine the best combination of instruments and sample replication which could be applied to the STRAT analyses. The information obtained from the test flights showed that the whole air sampler and the applied analytical techniques can provide reproducible data for the target compounds applicable to the STRAT missions. Detailed structures observed in vertical profiles of a several trace gases demonstrated the ability of the WAS to characterize the chemical variations in this region. In addition, we have identified several bromo- and iodocarbons in the low to sub-pptv level range using the GC/NICI/MS system and are in the process of developing calibrations for each compound.

The WAS was modified, using the previous configuration, from a 29- to a 49-canister manifold. This configuration was flown in the left superpod nose for the February 1996 STRAT flights. The WAS was redesigned as a 29-can manifold for deployment in the right superpod mid-body for the July and December 1996 STRAT flights.

During the January/February 1996 STRAT ER-2 flights distributions of trace gases showed characteristic profiles relative to potential temperature which could be related to chemical loss rates. Short lived gases, such as ethane, showed a rapid decrease in mixing ratio up to the 340 to 360 K surface, a more complex distribution in the 360 to 400 K region, and a latitude independent decay above 400 K. As expected, longer-lived gases (e.g., HCFC-22) were more uniformly distributed up to the 400 K level. Above this surface, clear latitudinal gradients are observed, with highest mixing ratios observed in the tropics and lowest mixing ratios at high latitudes. Profiles of selected species and correlations with CO_2 were examined for the region near the tropical tropopause to begin to evaluate transport rates in that region. Reasonably consistent vertical ascent rates were

obtained from estimated tropospheric growth rates of a new fluorocarbon replacement compound (HCFC 141b) as compared with ascent rates obtained from CO_2 distributions. Correlation of individual organic bromine species with CFC-11 were used to estimate the total organic bromine concentrations in air transported to the stratosphere. Current values are estimated at 17 to 18 pptv Br from this dataset. A variation of total organic bromine up to 22 pptv in the upper troposphere was observed. This increase was primarily due to enhancements in methylene bromide and bromoform, suggesting variability in transport and surface sources of some of the reactive organic bromine compounds.

Publications

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High-Sensitivity Fast-Response CO_2 Instrument

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Research Objectives

A fast-response CO_2 sensor was designed, built, and deployed for high-precision measurements in the stratosphere. There were two goals:

- Use the seasonal and long term changes in CO_2 concentrations to diagnose rates of transport of stratospheric trace gases on global scales.
- Provide the detection and quantitative determination of dilution for aircraft exhaust wakes in the atmosphere, allowing observations of pollutant concentrations (NO_x, small particles) to be used to define emission rates for aircraft in normal flight operations.

Summary of Progress and Results

Instrument Performance

The fast-response CO_2 sensor was first deployed during the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE, November 1992 - October 1993) and subsequently in the Airborne Southern Hemisphere Ozone Experiment (ASHOE, February 1994 - October 1994) and Stratospheric Tracers of Atmospheric Transport (STRAT, May 1995 - December 1996) campaigns. Long-term precision has been demonstrated to be better than 0.1 ppm over the 4-year period. The instrument has been extremely reliable, returning data of uniformly high quality for 96 of 97 flights (a single failure occurred when a static discharge re-formatted the flash card).

Stratospheric Transport

The measurements in SPADE demonstrated that the seasonal variations and long-term trend of tropospheric CO_2 concentrations propagate into the stratosphere, providing a temporal ensemble that may be used to define key aspects of global transport rates (Boering *et al.*, 1994, 1995; Wofsy *et al.*, 1994). In ASHOE and STRAT, CO_2 measurements showed that seasonal variations in tropospheric concentrations propagate simultaneously to the Northern and the Southern Hemisphere stratosphere.

Recent analysis of the observations showed that CO_2 data provide excellent determination of the true mean age of stratospheric air as well as a measure of the global mean upwelling velocity for the tropical source region. The analysis also demonstrated that the values determined for the true mean age are directly relevant for issues of societal importance, such as effects of stratospheric aviation on ozone.

Aircraft Exhaust Wakes

The instrument also provided unambiguous identification of ER-2 crossings of its own wake and quantitative emission indices for exhaust products. The data showed that estimates of emission rates from this jet engine, based on ground test data, were accurate.

Data for CO_2 provided the quantitative measure of dilution in the wake of the Concorde needed to derive emission indices from observations obtained during the ER-2 interception of the wake. These results showed extremely high emission rates for small particles, raising significant new issues for understanding effects of aviation on the stratosphere.

Publications

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Airborne Lidar Stratospheric Ozone and Aerosol Investigations

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Research Objectives

An airborne lidar is used to remotely measure the distribution of ozone (O_3) and aerosols in the lower stratosphere, and these observations are related to chemical and dynamical processes that can contribute to changes in stratospheric O_3, including those possibly associated with aircraft emissions. Observations of O_3 distributions are important in the direct detection of the spatial and temporal variations of O_3 changes, and the distribution and characteristics of stratospheric aerosols and polar stratospheric clouds (PSCs) are required to understand heterogeneous chemical processes that can lead to O_3 depletion. Both O_3 and aerosols can also be used as tracers of transport in the lower stratosphere and between the stratosphere and troposphere. To obtain remote measurements of O_3 and aerosols/PSCs in the lower stratosphere, an airborne Differential Absorption Lidar (DIAL) system is operated in a zenith mode from the NASA DC-8 aircraft on long-range flights from the polar regions to the tropics. The observed variability of O_3 and aerosols is related to the atmospheric processes that can contribute to O_3 changes.

Summary of Progress and Results

We have continued to investigate various transport processes in the lower stratosphere using the airborne DIAL O_3 and aerosol data obtained during the 1992 Airborne Arctic Stratospheric Experiment (AASE-II). Good agreement was found between the lidar observations of transport of mid-latitude air into the Arctic vortex and the "Contour Advection with Surgery" modeling of vortex dynamics. Additional analyses of transport out of the tropics across the subtropical barrier region using a combination of datasets including measurements from satellites and aircraft was completed. This research examined the build-up and removal rates for sulfate aerosols, the position and motion of the center of the reservoir, and the position and width of its boundaries. The aerosol and O_3 data from the airborne lidar provided the detailed spatial information needed to determine the structure and transport of the air in the lower stratosphere from the tropics to mid-latitudes.

A new airborne DIAL system for measurements of O_3 and multiple-wavelength aerosol profiles was constructed to provide a second DIAL system for possible future experiments requiring the fielding of two systems simultaneously on different aircraft. The new DIAL system has increased laser power (more than a factor of three) for improved stratospheric and tropospheric O_3 and

aerosol measurements. This system was initially flight tested on the NASA Wallops Flight Facility P-3 aircraft in October 1995, and it was subsequently integrated into the NASA Ames Research Center DC-8 aircraft prior to the start of the Tropical Ozone Transport Experiment and Vortex Ozone Transport Experiment (TOTE/VOTE) in December 1995.

Preparations were made for the TOTE/VOTE field experiment to use the airborne DIAL in investigations of O_3 and aerosol transport across the tropical barrier and across the Arctic vortex edge. This field experiment was conducted during two deployment periods starting in December 1995 and finishing in late February 1996. The airborne DIAL system performed very well during TOTE/VOTE under very difficult environmental conditions presented by the cold winter conditions in Alaska and Iceland and the poor cooling conditions on the DC-8. Simultaneous lidar data on aerosol distributions at 1064 and 622 nm and O_3 number density distributions were obtained by the airborne DIAL system on all flights during TOTE/VOTE, and the real-time data analysis and display was used during the DC-8 flights to guide the sampling strategy. Good agreement was found between O_3 profiles measured with the DC-8 DIAL and the NASA Goddard Space Flight Center (GSFC) O_3 lidar operated at the Mauna Loa Observatory on the island of Hawaii. The airborne DIAL data reduction for TOTE/VOTE has been completed, and the data have been archived.

A TOTE/VOTE Science Team meeting was held in Boulder, Colorado, in June 1996, and the initial results indicate that the filamentary O_3 structure observed with the DC-8 DIAL was associated with exchange across the Arctic vortex edge and between the tropics and mid-latitudes, and that this dynamics was in general agreement with the GSFC transport models. Investigations using airborne DIAL O_3 and aerosol data are underway to determine the amount of O_3 depletion in the Arctic vortex during the winter of 1995-1996 and whether the highest-altitude cirrus clouds observed in the tropics are above the tropopause, which would be important for improving our understanding of troposphere-stratosphere exchange processes. Joint investigations of the many topics identified at the recent Science Team meeting will be completed in 1996, and collaborative papers will be written and submitted for publication during the following year.

Publications

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The ER-2 Meteorological Measurement System (MMS)

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Research Objectives

The objectives are to instrument the NASA ER-2 high-altitude aircraft to measure accurate, high resolution, and fast-response *in situ* meteorological variables (temperature, pressure and winds), to participate in field studies, and to interpret the resulting data to advance our understanding of the lower stratosphere.

Summary of Progress and Results

Instrumentation

All subsystems of the MMS were modified between 1994 through 1996. The following modifications were driven by both external and internal forces in order to improve instrument performance (accuracy and precision) and to reduce weight.

- Development of a new data acquisition system in order to improve performance (accuracy and precision) and to minimize field operational requirement. The improvements include (1) the fundamental sampling rate increased to 65-Hz; (2) analog signals resolution increased to 16-bit; (3) storage media employed only flash memory; (4) in flight data processing generated exchange data during flight; and (5) reduced system weight by 20 lb.
- Improvement of static pressure measurement using quartz diaphragm transducer, which has a very low thermal expansion coefficient.
- Improvement of temperature measurement by installing a third temperature sensor forward on the fuselage station, well in front of other boundary flow perturbations.
- Improvement of navigational data using the Litton LN-100G lightweight ring laser gyro embedded GPS inertial (EGI) navigation system. The EGI has a full military specification, capable of receiving C/A and P/Y GPS code.

Field Missions

The ER-2 MMS successfully participated and returned quality scientific data supporting the following atmospheric research field campaigns:

- Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA)
  1. Four deployments to Christchurch, New Zealand (March through April 1994; May through June 1994; July through August 1994; September through October 1994) totaled about 45 flights.
  2. Four dynamic and radiation special studies in Christchurch, New Zealand.
  3. Ferry flight data generated as part of the Assessment Program (California - Hawaii - Fiji - New Zealand).
- Stratospheric Tracers of Atmospheric Transport (STRAT)

1. October 1994 latitudinal survey flight	Moffett Field, California.
2. April through May 1995 deployment	Moffett Field, California.
3. October through November 1995 deployment	Moffett Field, California; and Barbers Point, Hawaii.
4. January through February 1996 deployment	Moffett Field, California; and Barbers Point, Hawaii.
5. July through August 1996 deployment	Moffett Field, California; and Barbers Point, Hawaii.
6. September 1996 intercomparison mission	Moffett Field, California.

Publications

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NCAR Airborne Fourier Transform Spectroscopy and the Network for the Detection of Stratospheric Change

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Research Objectives

The objectives of this work are to use infrared spectroscopy to study the chemical and physical processes which control ozone in the stratosphere and upper troposphere. Using high resolution Fourier transform spectrometers, based on the ground and on aircraft, we obtain column amounts for ozone and a number of trace gases important to its chemistry, including NO, NO_2, HNO_3, HCl, HF, $ClONO_2$, as well as water and several tracers of atmospheric motions. As part of the Network for Detection of Stratospheric Change we make observations, participate in defining measurement and analysis procedures and help guide the NDSC through service on the Steering Committee and the working group on infrared instruments.

Summary of Progress and Results

We continued ground-based FTS observations which began in October 1994 at Sondre Stromfjord, Greenland (67°N, 50.7°W) until April 1995. During the SESAME campaign we recorded more than 26,000 high-resolution spectra. Analysis of the spectra using non-linear least squares fitting has produced column amounts for all the observation times for HCl, HF, O_3, HNO_3 and N_2O. These results have been deposited in the SESAME archive. Analysis and interpretation of the results, in conjunction with other observations made during SESAME, continues and has resulted in a number of presentations and the publications listed below.

We have received a Bruker model 120M Fourier transform spectrometer which will be sited at Thule, Greenland as part of the NDSC. We have conducted an extensive evaluation and acceptance procedure for the new instrument and are developing the mechanisms and procedures for remote operation. After intercomparison with the Bruker from the UK National Physical Laboratory and with the JPL MkIV interferometer we will locate the spectrometer at Thule to be ready for observations when the sun returns in spring 1997. We participated in the inter-comparison of spectral fitting algorithms in use by the various NDSC IR analysis groups.

We have completed our analysis of observations made during four field programs in polar wintertime regimes. A paper is in preparation which describes an integrated view of polar

stratospheric chemistry based on our column observations of HCl, HF, NO, NO_2, HNO_3, $ClONO_2$ and O_3. Column amounts are related to the potential vorticity at a given level and relationships established which allow vortex wide distributions to be calculated for nitrogen and chlorine families and individual chemical constituents.

Publications

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Measurement of Aerosol and Cloud Particles

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Research Objectives

The objective of this work was to integrate a new aerosol instrument, the Multiangle Aerosol Spectrometer Probe (MASP) onto the ER-2 payload, operate the MASP during the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) project, and analyze the results after the project. This was to include publishing papers on the design of the MASP; using measurements made in polar stratospheric clouds (PSCs) during ASHOE/MAESA to compare with PSC formation processes in the Arctic; compare the MASP observations with model simulations to better understand the formation processes in PSCs; analyze the index of refraction measurements to add understanding to the composition and phase of stratospheric aerosol; and collaborate with others in integrated studies from ASHOE/MAESA.

Summary of Progress and Results

The MASP is a new instrument which was designed and built under the auspices of the NASA High Speed Research Program and was flown for the first time on the ER-2 during the ASHOE/MAESA project. It counts and sizes particles in the nominal size range of 0.4 to 10 μm diameter and also provides estimates of the particle index of refraction over the size range of ~0.4 to 0.7 μm [Baumgardner *et al.*, 1995]. Analysis of selected results from the MASP in the stratospheric sulfate layer from latitudes of 70°S to 50°N suggest refractive indices from 1.40 to 1.42 [Baumgardner *et al.*, 1996] which are a little lower than is conventionally thought. In the altitudes from 8 to 20 km the refractive indices ranged from 1.34 to 1.46 and suggest the presence of non-spherical or absorbing particles at the lower altitudes.

Measurements in two PSCs in the outer region of the Antarctic vortex during ASHOE/MAESA show the onset of the clouds occurred near 193 K, 3° colder than nitric acid trihydrate (NAT) saturation. The onset temperatures, the smooth increase of volume with decreasing temperature, the inverse correlation of particle volume and enhanced NO_y (HNO_3 in the particles) with temperature suggest that much of these PSCs were composed of ternary solutions droplets [Dye *et al.*, 1996]. Furthermore, comparisons of the observations for the 28 July case with an equilibrium model of ternary growth are also highly supportive. However, in some regions the model is not

able to duplicate the variations in particle volume as a function of temperature suggesting that a solid phase may also be present. This is consistent with findings from the Ames wire impactors which detected the presence of some solid particles. The similarity of these Antarctic observations with earlier ER-2 observations in the Arctic help to unify our understanding of PSC formation processes.

During this period analysis and interpretation of earlier ER-2 observations continued including participation in describing the changes in size distribution which occurred as a result of the Pinatubo eruption [Jonsson *et al.*, 1996]. A Ph.D. dissertation by Katja Drdla working with our group shows that with a detailed microphysical model of PSC particles many of our PSC observations made in 1989 during the Airborne Arctic Stratospheric Experiment can be explained either with a ternary model of PSC growth or through mixed phases of ternary droplets with NAT particles [Drdla, 1996]. Continued collaboration with Stephan Borrmann of Johannes Gutenberg University, Mainz, Germany explores heterogeneous reactions on background and Pinatubo sulfate particle distributions and type I PSCs using particle measurements made in the Arctic during earlier campaigns. One of the results from the study is that the transition from PSCs composed of ternary solution droplets to NAT would reduce the rate of chlorine activation [Borrmann *et al.*, 1996a]. In another study [Borrmann *et al.*, 1996b] observations from ascents and descents of the ER-2 are used to show that some chlorine activation could be happening on cirrus particles. Our observations were also used in a number of other papers cited below.

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Four-Channel Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV)

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Research Objectives

The Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV) is designed to measure a variety of organic chlorine and bromine, and other trace species in the upper troposphere/lower stratosphere (UT/LS). ACATS-IV operates autonomously onboard the NASA ER-2 high-altitude aircraft. The instrument comprises four separate gas chromatographic (GC) channels each incorporating an electron capture detector (ECD) [Elkins *et al.*, 1996]. By selecting different GC columns, oven temperatures, and flow rates, the channels are currently configured to measure the following combination of species on channel 1, trace species, CFC-11, CFC-113, CH_3CCl_3, and CCl_4 are separated from air; similarly, on channel 2, N_2O and SF_6; channel 3, CFC-12 and halon-1211; and channel 4, H_2 and CH_4. A sampling frequency of 180 or 360 seconds (the latter for channel 2) is made possible with the use of a 2-position, 12-port gas sampling valve.

Summary of Progress and Results

The ACATS-IV instrument participated in the 1994 Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) aircraft campaign and the NASA Stratospheric Tracers of Atmospheric Transport (STRAT) mission during 1995-1996. The missions included several deployment locations in both hemispheres. Data for most of the species noted above were submitted to the data archive for nearly all flights in these missions. The most complete and precise datasets were obtained in the

last deployment of ASHOE/MAESA and all deployments of STRAT. These data are available on the two mission's CD-ROMs.

ACATS-IV measures about 80% of total organic chlorine and about 13-18% of total organic bromine entering the stratosphere. The remaining species of chlorine and bromine can be estimated from the observed species and their correlation with the unmeasured species which can be determined by either models or previously measured relationships. This permits the calculation of total organic and total inorganic chlorine [Woodbridge *et al.*, 1995] and bromine [Wamsley *et al.*, 1996]. ACATS-IV also measures species with a wide range of lifetimes from 4.5 years for CH_3CCl_3 to ~3200 years for SF_6. Good agreement was found in comparisons of ACATS-IV from ASHOE/MAESA and ATMOS satellite data obtained in November 1994 [Chang *et al.*, 1996a; b]. The measurement of sulfur hexafluoride (SF_6) permits the calculation of the mean age of the air mass because of its long atmospheric lifetime (~3200 years) and linear growth with time (~6.7% per year) [Geller *et al.*, 1996]. The correlation slope between long-lived species yields the ratio of their lifetimes. When the correlation includes a species for which the lifetime is well-established (e.g., CFC-11 at 55 years) [Elkins *et al.*, 1993], then the lifetime of the other species can be determined. The ACATS-IV measurements of H_2 and CH_4, when combined with separate ER-2 measurements of H_2O, constrain the total hydrogen budget in the lower stratosphere. Newman *et al.* [1996] reported on an extraordinary observation of nonlinear mixing of trace gases from ACATS and other instruments during the break-up of the polar vortex in SPADE.

The vertical profiles and correlations of this tracer suite can be used to estimate the transport mid-latitude air into the tropics in the lower stratosphere [Minschwaner *et al.*, 1996; Volk *et al.*, 1996]. The tropical stratosphere represents a very delicate region of the atmosphere, because it is where most of the ozone is produced and destroyed by sunlight. Chemicals from human activities (CFCs, Halons, etc.) that destroy ozone are transported high into the tropical stratosphere and are broken down into reactive chlorine and bromine species that further destroy ozone. The greatest amount of emission from aircraft and pollutants occur in the mid-latitudes. Therefore, exchange between the mid-latitudes and the tropics is very important in understanding the depletion of stratospheric ozone. Volk *et al.*, [1996] shows that mid-latitude air is entrained into the tropical lower stratosphere within about 13.5 months. Transport is faster in the reverse direction. Because exchange with the tropics is slower than global photochemical models generally assume, ozone at mid-latitudes appears to be more sensitive to elevated levels of industrial chlorine and bromine than currently predicted. Nevertheless, about 45% of air in the tropical ascent region at 21 kilometers is of mid-latitude origin, implying that emissions of nitrogen oxides from supersonic transport aircraft (SST) could reach the middle stratosphere. If atmospheric mixing was determined by simple diffusive transport, then the amount of air reaching the middle stratosphere would be larger than measured and would create more ozone destruction from future SSTs.

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Reactive Nitrogen Measurements on the ER-2 High Altitude Aircraft

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Research Objectives

A multi-channel instrument for the measurement of reactive nitrogen (NO_y) species is operated onboard the NASA ER-2 high-altitude aircraft. The instrument provides *in situ* measurements of NO, NO_2, and NO_y along each second of the flight path using a combination of techniques that include catalysis, photolysis, and NO/O_3 chemiluminescence. Each instrument channel is calibrated in-flight. For every flight, final mixing ratios of each measured species along the flight track are calculated and submitted to a data archive for the planning of subsequent flights and for later interpretation.

Summary of Progress and Results

The reactive nitrogen instrument has participated in the 1994 Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) aircraft campaign and the NASA Stratospheric Tracers of Atmospheric Transport (STRAT) mission. These missions included several deployment locations in both hemispheres. Data for NO and NO_y were archived for nearly all flights in these missions. Data for NO_2 were obtained with acceptable accuracy only poleward of 40° latitude.

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Microwave Temperature Profiler

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Research Objectives

The objectives of this task are to 1) determine tropopause altitudes from the temperature field during ER-2 and DC-8 aircraft flights to provide mesoscale atmospheric context for *in situ* measurements; 2) investigate the ever-present background of isentrope surface vertical displacements in the stratosphere and study their implications for polar stratospheric cloud (PSC) formation and evolution; 3) measure mountain wave structures in the stratosphere, to determine temperature excursions of air parcels moving through the topography-fixed waves; and 4) search for temperature field anomalies due to atmospheric filaments in the stratosphere so that modelers may gain insight into the dynamical processes producing latitude air movements.

The following activities were performed to achieve the above objectives: 1) reduce the size of an existing Microwave Temperature Profiler instrument aboard the DC-8, the MTP/DC8 instrument, and install it in an out-of-the-way location to enable the installation of other experiments on the airplane; 2) conduct MTP/DC8 observations during the TOTE/VOTE (Tropical Ozone Transport Experiment/Vortex Ozone Transport Experiment) mission; 3) conduct MTP/DC8 observations during the SUCCESS (Subsonic Aircraft: Contrail and Cloud Effects Special Study) mission; and 4) conduct observations with an MTP/ER-2 instrument (a microwave temperature profiler mounted in the ER-2 aircraft) during flights for the STRAT (Stratospheric Tracers of Atmospheric Transport) mission. For all these missions MTP data was compared with other measurements to study the atmospheric science objectives listed in the previous paragraph.

Summary of Progress and Results

The MTP/DC8 instrument has been reduced in size to 20% of its previous volume, and it has been mounted behind the mission manager's console. It no longer competes with any other DC-8 instruments for rack or window space. The MTP/DC8 now operates in a "turnkey" mode, which translates to lower cost for the support of future missions.

During TOTE/VOTE the MTP/DC8 temperature fields showed temperatures low enough for PSC formation at altitudes several kilometers above the aircraft on only two north polar vortex flights, assuming the air was not denitrified. On one of these occasions the DIAL (Differential Absorption Lidar) was not operating, so the presence of PSCs could not be confirmed; on the other occasion DIAL did not show PSCs, implying that the polar air may have been at least slightly denitrified.

Several TOTE/VOTE flights that crossed jet structures enabled the MTP/DC8 to document the temperature field at unprecedented high spatial resolution. On every occasion the tropopause "jumped," instead of moving smoothly, to a new value. The latitude transition between mid-latitude air and tropical air appears to be 6 degrees wide.

Tropopause "jumping" was also observed at mid-latitudes, and at the mid-latitude/polar latitude boundary. The lower-most 1 to 3 km of the stratosphere frequently undergoes vertical compression changes, causing lapse rate within the layer to change, which sometimes leads to tropopause jumps. This appears to be a newly noticed phenomenon, which may have implications for troposphere/stratosphere exchange, and it warrants further study.

The MTP/DC8 was flown during the SUCCESS mission, and documented dramatic altitude changes of isentrope surfaces and the tropopause in the vicinity of lenticular clouds. During flight in the vicinity of an anvil cloud the lapse rate was reliably -7 K/km within the anvil and different values outside.

The MTP/ER-2 instrument has been flown during the STRAT flights of 1995 and 1996. In addition to locating the tropopause altitude, which allows *in situ* measurements to be designated as either stratospheric or tropospheric, the MTP-derived temperature field has been used to identify a polar filament embedded in mid-latitude stratospheric air. The temperature signature revealed a "warm on top/cold on bottom" pattern for a 1.3 km thick layer in which extremely anomalous tracer mixing ratios were measured. Since the temperature anomaly associated with the filament may have been produced by the dynamical process that brought it to the location where it was encountered, additional study of this event may improve dynamical models for the latitudinal movement of filaments, which would add to our understanding of the exchange of air between different latitude regimes.

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Airborne Raman Lidar

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Research Objectives

The airborne Raman lidar uses Raman scattering to measure a variety of atmospheric traits simultaneously while flying on any of a number of large research aircraft. In the present configuration the system measures Rayleigh scattering, N_2 Raman scattering at three overlapping ranges, H_2O Raman scattering, and CH_4 Raman scattering. These measurement are used to deduce methane and water mixing ratio to an altitude of roughly 8 km above the aircraft and temperature and pressure to an altitude of 30 to 40 km above the aircraft. Flying in conjunction with other instruments on board the aircraft (in particular with an ozone lidar), this system may be used to address a number of scientific questions including the following:

- Are current stratospheric temperatures low enough to allow the formation of polar stratospheric clouds (PSCs)?
- Is the water vapor mixing ratio high enough to allow formation of PSCs?
- Has ozone loss occurred at the winter pole and how much?
- To what extent does mixing in and out of the winter polar vortex occur via the formation of filaments at the vortex edge?
- Does filamentation occur at the tropical mid-latitude boundary?

Generally speaking methane measurements can by used as a tracer of atmospheric motions so any number of additional questions about atmospheric dynamics may prove to be accessible via this technique.

Summary of Progress and Results

In 1994 the lidar was installed on the NASA C-130 aircraft operated by Wallops Flight Facility and a number of instrumental test flights were made including a long flight northward from Bangor, Maine to Baffin Island, Canada and back. Results of these flights will appear shortly in an article in *Applied Optics*. More recently, the system participated in the TOTE/VOTE measurement campaign on board the DC-8 aircraft operated by Ames Research Center. This campaign included participation by several different government labs and universities and

involved instrumenting the DC-8 with 2 lidar systems plus a variety of *in situ* instruments measuring gaseous trace constituents as well as aerosols. Over twenty experimental flights were conducted in the early and late winter of 1995-1996 in the northern polar regions as well as the mid-Pacific tropics. Figures 1 and 2 show results obtained on these flights for methane and water vapor. The first figure shows methane mixing ratio altitude profiles obtained on a flight from Eielson AFB, Alaska to Keflavik, Iceland crossing through the polar vortex. It can be seen that the observed methane values are lower inside the vortex and that the methane appears to be anti- correlated with the modified potential vorticity (MPV) both in agreement with theory. The region of low methane slightly to the east of the vortex may represent a filament of polar air stripping off from the vortex. Figure 2 shows water vapor measured on a flight from the polar region to the tropics. It is characterized by strong gradients in water vapor between polar air and mid-latitude/tropical air. Analysis of data from the VOTE/TOTE mission is still in progress.

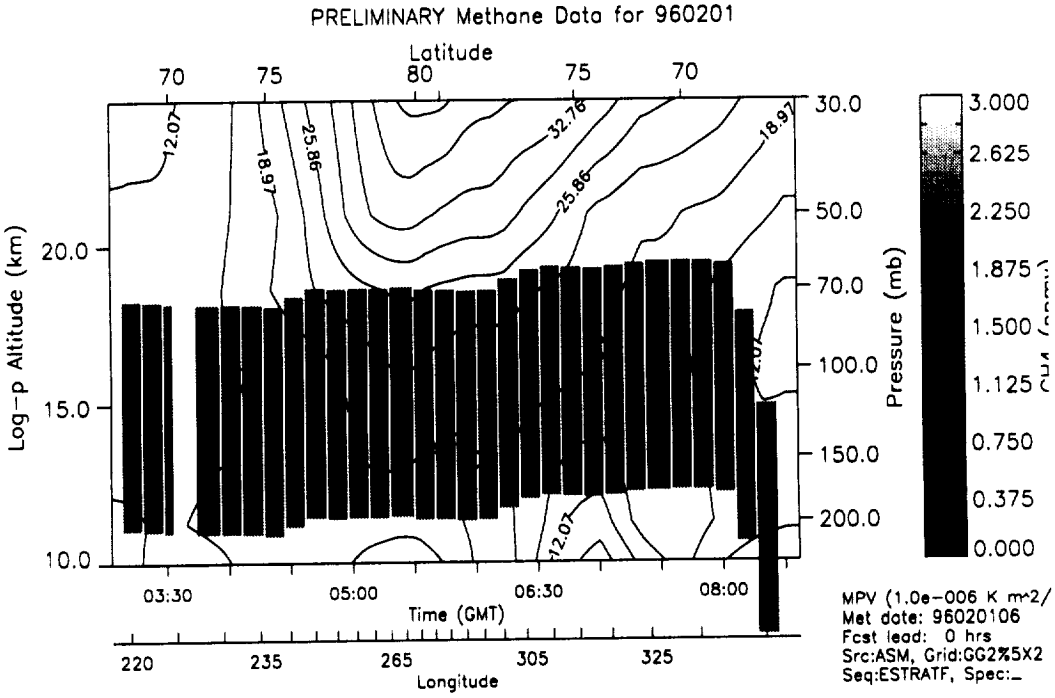

Figure 1. Water vapor and MPV for a flight from Alaska to Hawaii on 8 February 1996. Note the increasing values of water vapor as the aircraft enters the tropics.

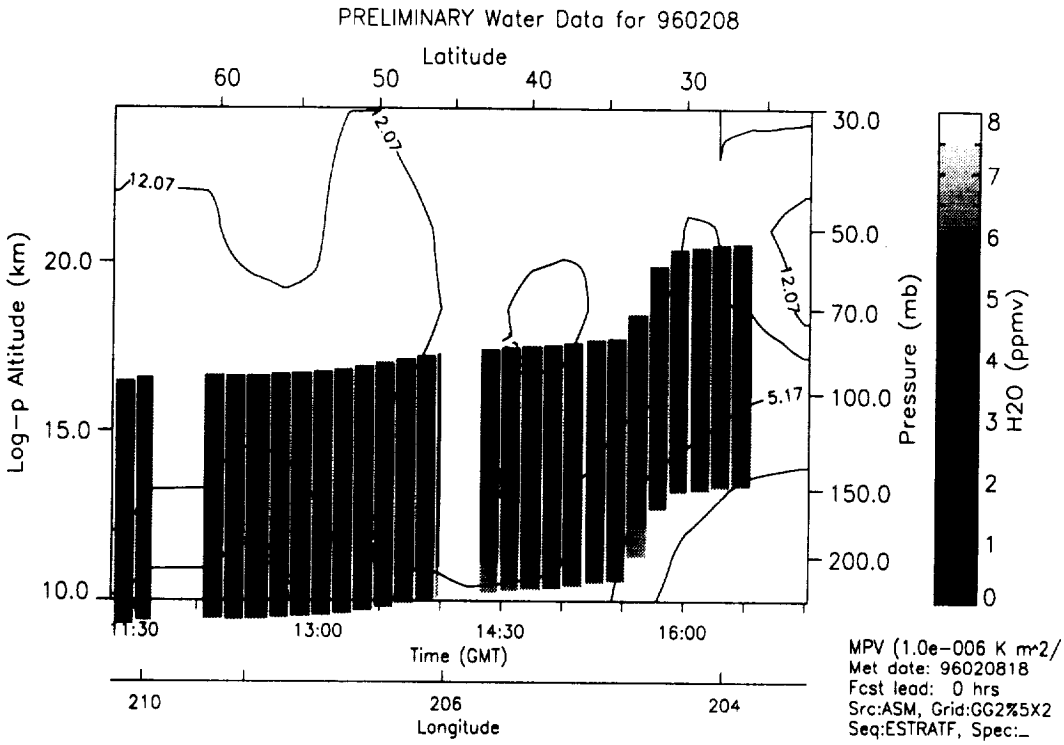

Figure 2. Methane and MPV versus altitude and position for a transit flight from Eielson AFB, Alaska to Keflavik, Iceland on 1 February 1996. The MPV values were obtained from the Goddard Data Assimilation Office.

Publications

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Aircraft Deployment Management

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Research Objectives

Two major campaigns were conducted during the reporting period (1994 through 1996): the Airborne Southern Hemisphere Ozone Experiment / Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) in 1994, and the Stratospheric Tracers of Atmospheric Transport (STRAT) in 1995 and 1996 (continuing through 1997). Both missions are jointly supported by the Upper Atmosphere Research Program, the Atmospheric Chemistry Modeling and Analysis Program, and the Atmospheric Effects of Aviation Project. The goals of the missions are to better understand production and loss mechanisms for stratospheric ozone, especially the cause of the mid-latitude ozone decline over the last 10 to 15 years, and to understand the exchange of air between the tropics and mid-latitudes to better assess the impact of a proposed future fleet of commercial supersonic aircraft.

Summary of Progress and Results

ASHOE/MAESA was conducted over the period of February through November 1994 in four three-week deployments using the NASA ER-2 aircraft. Through agreements implemented with the National Science Foundation and the Government of New Zealand, the primary deployment site was established at the U.S. Antarctic Program facilities at Christchurch, New Zealand. A second site was established through an agreement with the US Navy at Barber's Point Naval Air Station, Hawaii. The ER-2 carried 16 instruments to measure the abundances of reactive and inert trace gases, aerosols, temperature, pressure, winds, ultraviolet light, and temperature profiles. For flights specifically to study dynamics and radiation, some of the trace gas instruments were removed and an instrument that measures infrared radiation was added. A total of 45 flights were made accounting for close to 300 flight hours. Among the 45 flights, 26 were from Christchurch,

New Zealand, 5 were from Barber's Point, Hawaii, and 6 were transits between New Zealand, Fiji, Hawaii, and California. Also included were two full duration (8 hour) test flights north from Moffett Field in February, 5 short (2+ hours) test flights from Moffett Field between January and March and a northbound flight from Moffett Field in November, 1994. Thirty-two flights had the full payload, 11 had the dynamics and radiation configuration and 2 were test flights for individual instruments.

ASHOE/MAESA was successfully completed on 4 November 1994. An end of mission statement was released in January 1995. A science team meeting was held in San Diego in February 1995 to present and discuss the preliminary findings of the mission and to set publication goals. A CD-ROM containing the mission data was published and distributed to the science team in July 1995. It was decided that the coordinated papers would be published in a series of Journal of Geophysical Research Special Sections. The first such Special Section will appear shortly (late 1996).

The STRAT mission is an on-going series of mid-latitude and tropical deployments to obtain a seasonal dataset that continues the measurements started with the Stratospheric Photochemistry, Aerosols and Dynamics Expedition conducted in October/November, 1992 and April/May 1993. The mid-latitude flights are conducted from NASA Ames Research Center and the tropical flights from the NASA facility at Barber's Point Naval Air Station, Hawaii. Four deployments have been conducted to date: May 1995, October 1995, February 1996 and July/August 1996. Two science team meetings have been held in February 1996 and in July 1996. The first CD-ROM containing mission data from the first three deployments was published in September 1996.

Publications

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Diode Laser Absorption Spectrometer for Rapid Atmospheric Trace Gas Measurements

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Research Objectives

The ATLAS instrument was designed and built in the mid-1980s to measure stratospheric tracer fields from the ER-2 high-altitude research aircraft. During the decade of its operation ATLAS has primarily been used to measure the N_2O tracer field on numerous flights in several campaigns primarily focused on polar and mid-latitude processes in the stratosphere. Recently attention has turned to tropical dynamics, in particular the coupling between the mid-latitude stratosphere and the tropical "pipe" region.

Summary of Progress and Results

The NASA Ames Research Center Airborne Tunable Diode Laser Absorption Spectrometer (ATLAS) provides accurate atmospheric N_2O measurements on the ER-2 aircraft using tunable-laser, infrared spectroscopy. N_2O is a very long-lived tracer of stratospheric dynamics. Normally chaotic-appearing observations of molecular constituents of the atmosphere such as NO_y (total active nitrogen), CO_2, H_2O, CFCs and others are "smoothed" by constructing correlation diagrams of these observations plotted versus N_2O. These correlations then provide important chemical and dynamical diagnostic information on the state of the atmosphere.

During the Airborne Southern Hemisphere Ozone Experiment (ASHOE) in 1994 the correlation of NO_y vs. N_2O was observed to have a seasonal dependence. This correlation had already been observed, but only at one season, in the Southern Hemisphere in 1987. The correlation in the Northern Hemisphere however does not appear to have any seasonal dependence. The explanation for the observed Southern Hemisphere active nitrogen variation appears to be the precipitation of nitrogen compounds due to sedimenting Polar Stratospheric Clouds (PSCs) in the Southern Hemisphere polar winter. The Northern Hemisphere has far fewer PSCs due to a milder polar winter than in the Southern Hemisphere, so the absence of this effect in the Northern Hemisphere is expected.

During ASHOE and the follow-on Stratospheric Tracers of Atmospheric Transport (STRAT) campaign in 1995 and 1996 a comprehensive new dataset on CO_2 and N_2O in the Northern Hemisphere extending from the equator to 60°N latitude has been accumulated. Several important

results have emerged from this new and unique dataset. Briefly these new results can be summarized as tropospheric air carrying its normal seasonal cycle and secular trend of CO_2 continuously enters the lower tropical stratosphere and is rapidly (in ~1 month) transported to both hemispheres. The mean age of the observed mid-stratospheric air is ~6 years. Pollutant exhaust gases which will be deposited by proposed new stratospheric aircraft into the mid-latitude lower stratosphere will probably exceed the best current predictions by 30 to 100%. These results may have important implications for the impact of stratospheric aircraft on the ozone layer.

Publications

Boering, K. A., S. C. Wofsy, B. C. Daube, H. R. Schneider, M. Loewenstein, J. R. Podolske, and T. J. Conway, Stratospheric transport rates and mean age distribution derived from observations of CO_2 and N_2O, submitted to *Science.*

Keim, E. R., M. Loewenstein, J. R. Podolske, D. W. Fahey, R. S. Gao, E. L. Woodbridge, R. C. Wamsley, S. G. Donnelly, L. A. Del Negro, C. Nevison, S. Solomon, M. K. W. Ko, D. Weisenstein, and K. R. Chan, Measurements of the NO_y-N_2O correlation in the lower stratosphere: Latitudinal and seasonal changes and model comparisons, submitted to *J. Geophys. Res.*

Volk, C. M., J. W. Elkins, D. W. Fahey, R. J. Salawitch, G. S. Dutton, J. M. Gilligan, M. H. Proffitt, M. Loewenstein, J. R. Podolske, K. Minschwaner, J. J. Margitan, and K. R. Chan, Quantifying transport between the tropical and mid-latitude lower stratosphere, *Science, 272,* 1763, 1996.

Composition and Photodissociative Flux Measurement

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Research Objectives

The Composition and Photodissociative Flux Measurement (CPFM) experiment is designed to provide quantitative information about the photodissociation rate for a number of chemicals in the stratosphere, to provide diagnostic information about the radiation field present at ER-2 flight altitudes and to provide a direct measurement of the column amount of ozone above the aircraft. These measurements are used for the evaluation of the performance of models used to calculate the photodissociation rates for significant reactions in the stratosphere, to assess the role of clouds in controlling the rates of photodissociation in the stratosphere and as input to photochemical model simulations of the chemical data collected. Future research goals include the measurement of aerosol, ozone and nitrogen dioxide concentrations at, and below, the ER-2 flight level. The CPFM team also operates a Brewer Ozone Spectrophotometer at the ER-2 operational base to make Umkehr observations and accurate, traceable total ozone column measurements. The total ozone results are archived along with the other ER-2 data products on the NASA/Ames file server and published on the mission CD-ROM.

Summary of Progress and Results

The CPFM instrument was flown on all of the full-payload flights during SPADE, ASHOE/MAESA and STRAT. Scientifically useful results were obtained during all but a few flights. Because of the nature of the CPFM investigation which contributes a rather different kind of information to the program than the other sensors on board the aircraft, even the less successful flights have still provided interesting insights into the chemistry of the stratosphere.

Several very illuminating results that have come from the deployment of the CPFM among the instrument complement on the ER-2 include: 1) the verification of the approximate, absolute magnitude of the J-values for ozone photolysis to produce excited molecular oxygen, $O(^1D)$ [McElroy, 1995a; McElroy *et al.*, 1995b], 2) a direct determination of the J-value to photolyze NO_2 to produce NO at the aircraft position [e.g.: Gao *et al.*, 1996], 3) comparisons to albedos estimated from satellite estimates [op. cit.; McLinden, 1996b], and 4) total ozone column amounts measured from the ground and above the aircraft flight track [McElroy *et al.*, 1996]. The analyses of these results have demonstrated the need for radiation data to be collected along with the chemical constituent data, since the variability of ozone amounts and albedo along the flight track and with time will otherwise add a large unknown variance to all chemical model calculations.

Investigations of the correlation of the variations in OH and the J-value for the production of $O(^1D)$ from ozone photolysis have revealed an unexpectedly complex dependence of these parameters on the ozone column above the aircraft and the albedo below. This is a function of the degree to which the ozone amount below flight level is sufficient to 'shield' the local chemistry from the amount of cloud below when there is a significant partial column of ozone between the aircraft and the underlying, scattering surface.

One of the problems which existed in the use of the CPFM data is that the performance of the required quadrature to produce integral amounts representative of the full 4 * pi sphere illuminating the atmosphere in the vicinity of the aircraft depends on the [poor] assumption that the two spots in the hemisphere which are sampled by the CPFM field of view can be used to estimate the complete integral over the hemisphere below the aircraft.

For the last mission of the STRAT program, a CCD camera and data acquisition system was successfully flown in the CPFM wing pod. The camera produces digital images of almost the full hemisphere below the aircraft. These images will be used to estimate the temporal and spatial distribution of albedo changes below the aircraft and around the horizon and their contribution to the variability of the CPFM data. These camera images will be used to calculate more suitably weighted values for determining the global J-values and should lead to J-values with a somewhat smaller point-to-point variance and also with a covariance with respect to the modeled quantities which is smaller. This is because the weighting with respect to the image intensity detail should eliminate the over-domination of the surface albedo measured in the small spot included in the instrument field-of-view in the nadir direction and the domination of the pi steradians near the horizon by the one limb point measured. These measurements should be of particular value in the upcoming POLARIS Arctic flights.

Publications

Gao, R. S., D. W. Fahey, R. J. Salawitch, S. A. Lloyd, D. E. Anderson, R. DeMajistre, C. T. McElroy, E. L. Woodbridge, R. C. Wamsley, S. G. Donnelly, L. A. Del Negro, M. H. Proffitt, R. M. Stimpfle, D. W. Kohn, P. A. Newman, M. Loewenstein, J. R. Podolske, E. R. Keim, J. E. Dye, J. C. Wilson, and K. R. Chan, Partitioning of the reactive nitrogen reservoir in the lower stratosphere of the Southern Hemisphere: Observations and modeling, submitted to *J. Geophys. Res.*, 1996.

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Airborne Aerosol Lidar

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Research Objectives

The overall objective of this research is to use lidar to study the evolution and dispersal into the atmosphere of aircraft exhaust aerosols in the region from just behind the engine exit plane to distances several tens of kilometers downstream of the aircraft. To date, the program has used ground-based lidar systems at NASA Langley Research Center to obtain high vertical and spatial resolution aerosol backscatter measurements behind the Langley Boeing 737-100 Transport Systems Research Vehicle (TSRV) aircraft. Since exhaust aerosols are good tracers of fluid motion, the backscatter data can be used to evaluate fluid dynamics computer models of the wake vortex and near-field regime. Backscatter data collected simultaneously at multiple wavelengths can provide information on changes in the aerosol size distribution (e.g., the formation of new sulfate aerosols) that may have significant implications for aerosol-catalyzed heterogeneous chemical processes.

Summary of Progress and Results

This research program was initiated in late 1994 with test flights of the TSRV past the Langley Aerosol Research Branch ground-based lidar site, which has been operated for more that twenty years to measure properties of the stratospheric aerosol layer. The TSRV is outfitted with real-time differential GPS (Global Positioning System) navigation software, which allows the aircraft to be flown precisely over the lidar site or through waypoints offset from the site. Two modes of operation have been used to date. In one mode, the TSRV is flown in a direction perpendicular to the local wind through waypoints upwind of the lidar site. The backscatter from the exhaust aerosols is then measured in quasi-transverse planes through the aircraft wake vortices as the vortices are advected over the lidar site by the wind. In the second mode, the TSRV is flown directly over the lidar site in a direction parallel to the local wind, and backscatter from the exhaust aerosols is measured continuously downstream of the aircraft until the vortices move out of the lidar field-of-view.

Two ground-based lidar systems are being used in the program. One system operates in a fixed zenith-viewing mode with a vertical resolution of ~3 meters. This system has a 1.2-meter diameter collecting telescope, enabling high signal-to-noise operation, and can be operated simultaneously at wavelengths of 0.355, 0.532 and 1.064 μm. Two interleaved 10-Hz Nd:YAG lasers have been

used for these aircraft aerosol measurements, allowing data collection at a 20-Hz rate. The second lidar can be scanned out to zenith angles of 10 degrees, but has a smaller telescope (0.35-meter diameter) and poorer vertical resolution (7.5 meters), and has been operated at a single wavelength of 1.064 μm.

Successful experiments have been conducted with the TSRV in March and July 1995, and in February and March 1996, with major improvements made in the experimental procedure and in data collection/analysis software. Some coordinated flights were made with the Wallops T-39 aircraft which carried *in situ* instruments from Langley (Bruce Anderson) and the US Air Force Phillips Laboratory (Al Viggiano). During these parallel-to-the-wind flights, the T-39 trailed the TSRV by approximately 6 kilometers (1 minute), and the ground-based lidars collected data during the intervening period and again after the T-39 had safely passed the site. In the February 1996 experiment, *in situ* TSRV exhaust aerosol measurements were also made on the ground at Langley by the University of Missouri-Rolla group (Phil Whitefield/Don Hagen), detailed chemical analysis was performed on samples of TSRV fuel, and a third aircraft (the Langley OV-10A) was operated to obtain high-resolution temperature and wind data in the vicinity of the TSRV flight track. Data analysis is now in progress, in collaboration with modeling groups from Aerodyne Research, Inc., Continuum Dynamics, Inc., and West Virginia University.

Publications

None

Ames Wire Impactor and Replicator Applications

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Research Objectives

The objective is to determine size, shape, phase and composition of aerosol and cloud particles in the stratosphere (including types I and II polar stratospheric clouds) and in the upper free troposphere (including aircraft contrails). This is being accomplished by collecting atmospheric aerosol particles with wire impactors and ice crystals with Formvar replicators. The instruments are inletless devices designed for operation on NASA ER-2 and DC-8 research aircraft. They permit the collection of aerosol and cloud particles in the diameter range 0.01 $\mu m<R<500\ \mu m$. The collected particles are retained to be examined in a laboratory by optical and electron microscopy to determine their size morphology. Specific reactions and X-ray energy dispersive analysis permit investigations of the chemical/elemental composition of individual aerosol and cloud particles.

Summary of Progress and Results

- Frozen and liquid sulfuric acid particles coexist inside the southern polar vortex. Apparently, some of the smaller stratospheric aerosol particles contain a large enough fraction of sulfuric acid to depress the frostpoint by $\Delta T = -1.86$ iM (M = molarity, I = Van't Hoff factor) below the frostpoint of larger, more dilute particles.
- Type II PSC particles of solid and hollow columns, and plates were measured in the Antarctic stratosphere. Even though they exhibit a small surface area (< 10% of the background aerosol), their relatively large size can play an important role in the denitrification and dehydration of the stratosphere.
- The emission index of soot aerosols of a Concorde supersonic aircraft is EI(soot) = 0.07 ± 0.05 grams soot per kg of fuel burned.

Applying EI(soot) = 0.07 g (kg fuel)$^{-1}$ to current fuel consumption indicates that the present soot concentration in the lower northern stratosphere (approximately 0.5 ng m^{-3}) is mainly due to aircraft emissions. Thus, soot aerosol is a unique tracer of aircraft exhaust emissions.

Applying EI(soot) = 0.07 g (kg fuel)$^{-1}$ to projected fuel consumption suggests a three-fold increase of stratospheric soot burden within 20 years.

- A strong gradient of soot aerosols exists between the Northern and Southern Hemispheres. This implies that stratospheric residence timeof soot particles (e-folding of 1.1 year) is significantly shorter than is the mixing time between the hemispheres.
- Soot is a small fraction (one part in 1.E3 to 1.E4) of the lower stratospheric aerosol.
- Subsonic aircraft exhaust aerosol is characterized by an abundance of small (modal radius < 10 nm) spherical particles. The larger of them contain sulfur, a proxy for sulfuric acid. Preliminary results indicate an emission index EI(H_2SO_4) = 0.2 g (kg fuel)$^{-1}$.
- The 1991 Pinatubo volcanic eruption increased the particle surface area of stratospheric aerosols up to 50-fold and the particle volume up to two orders of magnitude.
- For some time after the 1991 Pinatubo eruption, volcanic ash of non-spherical particles was a significant fraction of the stratospheric aerosol. This may have caused an ambiguity in lidar backscatter depolarization signals, which generally are interpreted as being caused by Type II polar stratospheric cloud particles.

Publications

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In Situ Measurements of Tracer Species Aboard the DC-8 in Support of the TOTE and VOTE Experiments

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Research Objectives

The Langley airborne spectrometer system was deployed aboard the Ames DC-8 during the Tropical Ozone Transport Experiment (TOTE) and the Vortex Ozone Transport Experiment (VOTE) to provide high-precision measurements of CO_2, CO, N_2O, CH_4, and H_2O(v) for use in studying atmospheric structure and transport processes, identifying air mass origins, and validating data from onboard remote sensing systems.

Summary of Progress and Results

The Langley spectrometer system is comprised of: 3 cryogenically-cooled infrared tunable diode laser/detector pairs for differential absorption measurements of CO, CH_4, and N_2O concentrations within ambient air drawn through a long-path length sample cell; a constant pressure, dual-cell non-dispersive infrared spectrometer for CO_2 assay; and a room-temperature tunable diode laser/detector pair for H_2O determinations along an external path. These instruments were installed aboard the DC-8 in November 1995 and, with a few exceptions, provided good quality, fast-response measurements during both the TOTE and VOTE flight series. Post-mission analyses indicate the instruments performed with nominal precisions of 1% (CO), 0.1% (CH_4), 0.1% (N_2O), < 0.1% (CO_2) and < 0.5% (H_2O(v)). Five-second averages of the CO_2, CO, CH_4, and N_2O data from both missions and H_2O(v) data from VOTE were prepared and submitted to the archive by late March, 1996. Water vapor data from TOTE were of questionable quality due to electrical and optical feedback problems and thus were not submitted to the archive. TOTE H_2O(v) data may be obtained for limited and specific time periods by placing requests to the investigators.

Though the topics of VOTE and TOTE analyses are just now coming into focus, the LaRC tracer species data will provide essential information to a number of important studies. For example, the CH_4 measurements will be used as reference values at the DC-8 altitude for the GSFC methane lidar system. Measurements of CO_2 and H_2O(v) recorded during DC-8 encounters of its own exhaust plume will be used to calculate emission indices for other species measured by *in situ* techniques aboard the aircraft. Tracer measurements recorded in convective outflow will help delineate lightning from vertical transport-produced enhancements in NO_x concentration.

Similarly, the combination of CO, CH_4, and CO_2 measurements with N_xO_y observations should allow us to determine if flight corridors crossed during TOTE/VOTE exhibit enhancements of aviation related pollutants. The data will also used to identify the presence and characteristics of vortex filaments encountered at DC-8 altitudes during the mission.

Publications

TOTE/VOTE manuscripts are in preparation and will be submitted to journals in early 1997.

Radiative Flux Measurements

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Research Objectives

Our objectives were to demonstrate the ability to make balloon flights with a total-direct-diffuse radiometer (TDDR) and obtain a high-altitude multi-spectral extinction profile from which a profile of ozone concentration could be obtained; using the same measurements of spectral extinction, determine the optical characteristics of the stratospheric background aerosol; develop and refine cloud and aerosol retrieval methods using solar and infrared radiative flux measurements.

Summary of Progress and Results

- Two STRATEOLE balloon test flights were conducted, with a TDDR payload collecting ozone and volcanic aerosol data.
- Inversion algorithms were developed to retrieve the ozone profile from multi-spectral visible extinction data. The retrieved ozone profile is the first of its kind using visible radiometry. Simultaneous retrieval of aerosol spectral extinction results from this method.
- An infrared 2-channel retrieval algorithm, first developed for the AASE II DC-8 dataset, was refined, and applied to cloud radiation data collected during TOGA-COARE and ASTEX, to derive cloud thickness and emissivity.
- An inversion technique to estimate the vertical profile of aerosol optical characteristics from airborne measurements of upwelling and downwelling spectral solar hemispherical fluxes was developed. This technique was used to obtain the spectral distribution of aerosol optical depth, single scattering albedo, asymmetry parameter, and scattering phase function.

Publications

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Aircraft Measurements of the ALIAS Instrument

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Research Objectives

The Aircraft Laser Infrared Absorption Spectrometer measurements task has as its primary objective the collection of data on the concentrations, distributions, and variabilities of the minor and trace species in the stratosphere and troposphere. The *in situ* laser absorption spectrometers ALIAS (ER-2) and ALIAS-II (RPV, balloon) provide measurements of several gas concentrations as part of multi-instrument aircraft and balloon payloads flown for NASA missions, and for satellite correlative measurements (e.g. Upper Atmospheric Research Satellite (UARS)). The instruments use tunable diode lasers in the 3-10-μm wavelength region to measure gas concentrations in multi-pass optical cells either contained in a flow vessel (ALIAS) or in an open-path deployed cradle (ALIAS-II). The instruments have demonstrated capability for : N_2O, CH_4, HCl, CO, and NO_2, at the tens-of-parts-per-trillion levels, with capability to measure other gases within the 3-20-μm wavelength region; ALIAS is a 4-channel instrument, ALIAS-II is a 2-channel instrument.

Summary of Progress and Results

Over the last three years, the ALIAS instrument has flown as part of the payload of the ER-2 aircraft in several major missions: the 1993 Stratospheric Photochemistry Aerosols and Dynamics Experiment (SPADE) out of Moffett Field, CA; the 1994 Airborne Southern Hemisphere Ozone Expedition (ASHOE/MAESA) out of Moffett Field, Hawaii, Fiji, and New Zealand; and the ongoing 1995/6 Stratospheric Tracers of Atmospheric Transport (STRAT) mission out of Moffett Field and Hawaii.

The temporal and latitudinal extent of this series of missions has allowed a systematic study of heterogeneous chemistry related to the Mt. Pinatubo aerosol loading. ALIAS measurements of hydrochloric acid (HCl) concentrations in the lower stratosphere from 1991 to 1996 reveal that its abundance relative to total inorganic chlorine (Cl_y) has evolved upwards from HCl/Cl_y=0.5 in late 1991 to 0.8 in 1996. The observed fraction is anticorrelated with aerosol particle surface area, which has been diminishing since the massive increase associated with the June 1991 volcanic eruption of Mt. Pinatubo. Photochemical model calculations incorporating new laboratory-

measured chlorine activation rates show that air parcels with high aerosol loading exposed to temperatures below 205 K experience enough chlorine activation to drive the HCl/Cl_y ratio below 0.6 as observed, the balance of Cl_y being in chlorine nitrate, $ClONO_2$.

During the SPADE campaign of May 1993, ALIAS provided measurements of HCl, N_2O, and CH_4, and produced the first measurements of NO_2 from the ER-2 aircraft, using the direct laser absorption technique. The large differences between the measured concentrations and values predicted by gas-phase models confirmed the role of the heterogeneous conversion of NO_x to HNO_3 on sulfate aerosols at mid-latitudes. Furthermore, the SPADE flight series provided the opportunity to record for the first time the diurnal variation in NO_2 at the aircraft altitudes, and test the active nitrogen partitioning through the NO_2 /NO ratio measurements.

For the ASHOE/MAESA campaign of 1994, a new capability for measuring carbon monoxide (CO) was added in place of the NO_2 channel. CO concentrations were mapped over a wide range of latitude and season, to reveal a large decrease in tropospheric values from northern to southern latitudes. Furthermore, when measured CO, NO, and O_3 are used to calculate HO_2 /OH ratios, the calculated ratio agrees very well with direct measurement of OH and HO_2 over a factor of 5 change in the ratio. The Northern Hemisphere AASE-II studies of low temperature polar processing on PSCs were extended to the southern hemisphere vortex edge, and the new HO_x measurements were used in conjunction with those of HCl and ClO to further constrain the mechanisms of chlorine activation and recovery. Air parcels severely depleted in O_3 were encountered, and the high HCl observations served to confirm the expected conversion of Cl_y to HCl. This campaign also provided opportunities to sample the Concorde plume, and to intercompare with the ATMOS instrument aboard the Space Shuttle.

During the ongoing STRAT mission, ALIAS is producing measurements of N_2O, CH_4, CO and HCl. STRAT measurements of HCl at mid-latitudes show HCl/Cl_y values of about 75%, somewhat higher than the November 1994 ATMOS intercomparison, and consistent with the lower surface areas of about 1 :m^2/cm^3 measured by the FCAS experiment. Tracer measurements of N_2O and CH_4 are being used in combination with those of CO and CO_2 to characterize the air parcel origin and history for testing developing concepts of atmospheric transport.

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NO and NO_y Measurements in the Stratosphere

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Research Objectives

Reactive nitrogen species are important to the chemistry of O_3 throughout the atmosphere. We are interested in the measurement of NO, NO_y, and O_3 in the upper troposphere and lower stratosphere, especially, where reactive nitrogen species have not been thoroughly measured, yet where they may be subject to the influence of aircraft emissions. This is also a region where NO_x is relatively long-lived, so sources such as aircraft and lightning, which are present in this region but which are not large in terms of overall magnitude, can have a disproportionate effect. Among the topics we address with our measurements are the following: near-field exhaust studies, heterogeneous interconversion among NO_y species, the abundance of particulate NO_y, lightning as a source of NO_x, and the climatology of NO_x and NO_y. Also, there are issues surrounding the measurement of NO_2 and NO_y, and these are addressed with laboratory studies and in-flight diagnostic tests.

Summary of Progress and Results

Five papers were published, most during the early portion of the period:

- Weinheimer *et al.* [1994] summarizes the climatologies of NO_x, NO_y, and other species during AASE II. The meridional distribution of NO_x displayed no significant altitude gradient but showed a substantial latitude gradient with higher values at lower latitudes. Overall levels were similar to those of AASE I but substantially smaller than those of TROPOZ II.
- Zheng *et al.* [1994] is an analysis of aircraft exhaust plumes accidentally encountered during AASE II. Emission indices for NO_x were found which compared well with published values. The index found for CO was higher than the published value by a factor of 5. It was also found that reactive nitrogen other than NO_x accounted for only a very small percentage of the observed increment in NO_y.
- Zheng *et al.* (in press) focuses on the various small and large scale increases in NO_y and, using measurements of tracer species, determines the origin of the increases. Although numerous aircraft emission spikes were identified, an aircraft corridor effect was not detected in this analysis.
- Folkins *et al.* [1994] is a 3D model study of NO_x and NO_x/NO_y ratios measured during AASE II on the DC-8. It focuses on a comparison of measured NO_x/NO_y ratios to those computed by a semi-Lagrangian chemical transport model. The model is run with each of three sets of

reactions: (a) gas phase only, (b) gas phase plus the $N_2O_5 + H_2O$ reaction on sulfate aerosol, and (c) gas phase plus the $ClONO_2 + H_2O$ aerosol reaction. The gas phase runs generally gave NO_x/NO_y ratios that were too high (especially for the moderately sunlit March flights), while the runs including the $ClONO_2$ aerosol reaction generally gave too low values of the ratio. The runs including the N_2O_5 aerosol reaction generally agreed best with the measurements, but the modeled ratio was occasionally too low in this case.

- Another paper by Folkins *et al.* [1995] describes the AASE II flights to and from Tahiti, where an abrupt (~1 km) transition in air masses was encountered near the subtropical jet, with low values of NO_x, NO_y, and O_3 on the equatorward side of the transition. Simulation of the NO_x/NO_y ratio, using a model that is successful in mid-latitude air, drastically overestimates the ratio in tropical air. The model converts NO_x to HNO_3 via the $NO_2 + OH$ reaction (plus the slower N_2O_5/aerosol pathway), and it does so very slowly because low O_3 concentrations and cold temperatures cause most of the daytime NO_x to be present as NO. Thus the model NO_x/NO_y ratio is much higher than observed. It is important to resolve this discrepancy because a model with O_3 and NO_y that agree with observations will nonetheless drastically overpredict O_3 production rates and OH concentrations in the upper tropical troposphere.

From November 95 through February 96 we participated in the TOTE/VOTE missions, and from February through May 96 we participated in the SUCCESS project. Between the two projects we made measurements on 39 flights of the DC-8. Using a 3-channel probe, we measured the following in our standard configuration: (a) NO and O_3 through an aft-facing inlet at close-to-ambient temperatures, (b) gas phase NO_y through an aft-facing inlet at an elevated temperature and (c) gas phase plus particulate NO_y (with enhancement of the particles via anisokinetic sampling) through a forward facing inlet at the same elevated temperature as the aft-facing inlet. To address our concerns about the NO_y measurement, on a number of flights we measured the interference from HCN, in the presence of ambient and, alternately, added water vapor. We found that converters can be selected for which the HCN conversion is small (<10%) and that this interference is reduced by the addition of 500 ppmv of water to the sample flow. Just prior to these missions we investigated possible interferences in the measurement of NO_2 from $ClONO_2$, N_2O_5, and HO_2NO_2. The interferences from $ClONO_2$ and N_2O_5 were found to be small, while the interference from HO_2NO_2 was found to be 30% in the laboratory setup, though perhaps half of this occurred in plumbing that would not be part of an aircraft inlet.

We saw a number of interesting cases during the TOTE/VOTE and SUCCESS flights. These include (a) elevated levels, at times, of particulate NO_y with particulate amounts up to and exceeding simultaneously measured gas phase levels, (b) instances of elevated NO_x in the vicinity of electrified clouds, one being an extended transit through an electrically active mesoscale convective system, (c) interesting transitions between mid-latitude stratospheric and tropical tropopause air in north-south transit flights and (d) numerous measurements of aircraft exhaust under a variety of conditions, such as polar stratosphere versus tropical troposphere, with and without persistent contrail, and at varying distances behind the source aircraft. The measurements from the TOTE/VOTE and SUCCESS flights will enable substantial progress toward our objectives listed above.

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STRAT Campaign: ER-2 Participation

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Research Objectives

Stratospheric Dynamics: In the stratosphere, the distribution of ozone reflects both photochemistry and dynamics. The fundamental questions to be addressed by this research are: Do we understand how long-lived species are transported in the stratosphere? How do the dynamics of the stratosphere change as a function of season, altitude, and latitude? Answers to these questions are required to understand how the proposed High Speed Civil Transport may perturb stratospheric ozone. *In the stratosphere, simultaneous observations of long-lived tracers (such as water vapor) can provide important mechanistic information on how air enters and exits the stratosphere as well as how the rate of mixing within the stratosphere depends on latitude, altitude and season.*

Upper Tropospheric Photochemistry: Ozone in the upper troposphere is an important green-house gas. Additionally, ozone production in the upper troposphere may be an important global source of tropospheric ozone, which in turn determines the oxidative power of the entire troposphere. Ozone is produced in the troposphere through the coupling of odd hydrogen free radicals (OH and HO_2), with nitric oxide (NO) and carbon monoxide (CO). Three questions establish the objectives of this research: Do we understand the sources and sinks of OH and HO_2? Do we understand the sources and sinks of NO? Do we understand how the production rate of ozone depends on the concentrations of these free radicals? Answers to these questions are required to understand how the present fleet of civilian aircraft may have changed upper tropospheric ozone. *To test our understanding of tropospheric photochemistry, the STRAT campaign will provide the first simultaneous measurements of OH, HO_2, NO, and CO in the upper troposphere.*

Summary of Progress and Results

OH and HO_2: The first measurements of OH and HO_2 have been made in the middle and upper troposphere. This fulfills a long-standing need of the atmospheric chemistry community. The STRAT measurements now include observation at mid latitudes and in the tropics during fall, winter, and summer. Analysis of this dataset is ongoing but, in general, the concentrations of OH, HO_2, and NO in the upper troposphere are all larger than expected. This suggests that the production rate of ozone is larger than expected. Shown in Figure 1 are measurements of HO_2

obtained simultaneously with observations of NO (D. W. Fahey and R. S. Gao, NOAA Aeronomy Laboratory) as the sun rose in the upper troposphere on 3 August 1996. The dataset is preliminary, but it shows the performance capabilities of both instruments. The measured concentrations of OH, HO_2 and NO are all zero prior to sunrise as expected due to the lack of sunlight that is required to produce these species from their source molecules. The observed change in the radical concentrations is an important clue for determining the source molecules and this analysis is just getting underway. Additionally, with the extensive dataset, we should also be able to investigate, empirically, the response of ozone production rates to variations in the concentration of NO, CO and the HO_x source gasses.

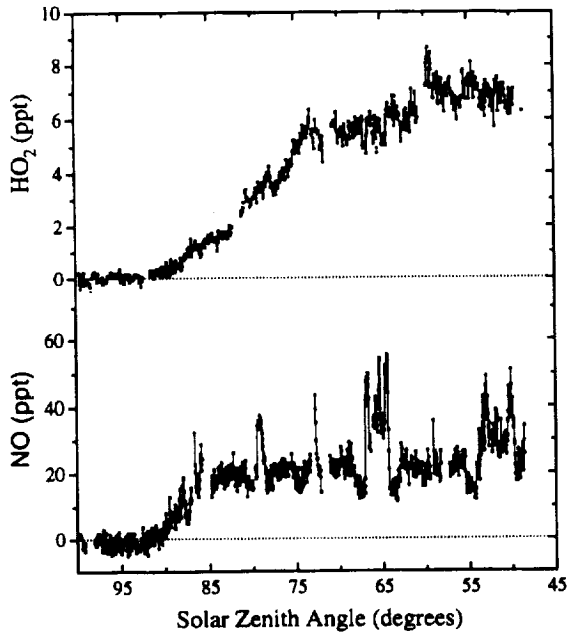

Figure 1. Preliminary data for NO (measured by D. Fahey and R. S. Gao of the NOAA Aeronomy Laboratory) and HO_2 measured on 3 August 1996, near Hawaii at 12 km. Both NO and HO_2 are zero before sunrise. NO is produced immediately after sunrise due to the photolysis of NO_2. The source species responsible for HO_2 production are not known. Together, these two radicals control the production of ozone in the upper troposphere.

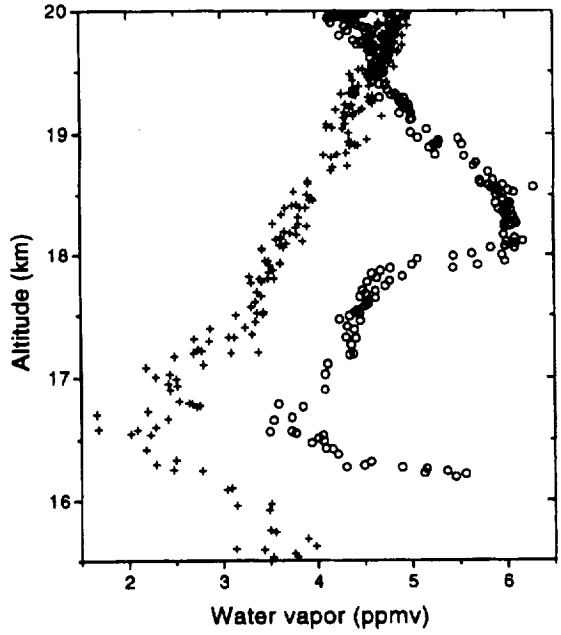

Figure 2. Water vapor profiles at the equator for STRAT flights on 5 November 1995 (o) and 13 February 1996 (+). The tropopause is near 16.5 km on both flights. From the upward propagation of the seasonal cycles of water vapor in the tropics, we can provide estimates of average vertical velocities in that region as a function of altitude and season.

Water Vapor: Observations of the seasonal cycles of H_2O with respect to other tracers have been made over a range of latitudes from the equator to very high mid latitudes. These data provide estimates of transport parameters, for both vertical and horizontal diffusion as well as the rate of diabatic ascent in the tropics. An example is shown in Figure 2. The moisture content of air entering the lower stratosphere in the tropics varies seasonally due to the variation of tropopause temperature. In February, the tropical tropopause reaches its coldest temperatures (< 190 K) and desiccates the air entering the stratosphere to less than 2 ppm. Conversely, in July/August, the

tropopause is warmest and air entering the stratosphere is wettest. These alternating minima and maxima in water vapor mixing ratio then propagate upward as air in the tropical lower stratosphere rises. Observation of the propagation of the season cycle thus provides a direct measurement of the ascent rate.

Publications

None

Aerosol Measurements from the ER-2 in SPADE (Stratospheric Photochemistry, Aerosol and Dynamics Expedition) ASHOE/MAESA (Airborne Southern Hemisphere Ozone Expedition/Measurements for Assessing the Impact of Stratospheric Aircraft) and STRAT (Stratospheric Tracers of Atmospheric Transport)

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Research Objectives

Aerosol particles play an important role in stratospheric chemistry. Heterogeneous chemical reactions occurring on the surfaces of particles influence the partitioning of reactive nitrogen species and therefore affect the abundance of chlorine and hydrogen radicals. Since many of these species are important in ozone loss, it is important to understand the composition and abundance of the aerosol and the factors controlling them. Sulfate aerosol also serve as nuclei for the formation of polar stratospheric clouds and can serve as a tracer of atmospheric motions. We characterize the size distribution of particles in the 0.08 to 2.0 micron diameter range with the Focused Cavity Aerosol Spectrometer (FCAS). The FCAS uses an optical bench built by Particle Measuring Systems and is designed and constructed at the University of Denver. The Condensation Nucleus Counter II (CNC II) measures the concentration and volatility of stratospheric particles in the 0.008 to 2 micron diameter range. The CNC II also contains an impactor sampler which collects particles for later analysis. The measurements and collections are done on the NASA ER-2 high altitude aircraft. Aerosol and other ER-2 measurements are analyzed to study the following topics: a) the impact of aerosol on the chemistry of the lower stratosphere. b) the factors affecting the abundance of aerosol particles in the upper troposphere and lower stratosphere c) polar stratospheric cloud formation d) the nature and quantity of particles emitted by aircraft and their likely effects e) the impact of volcanic eruptions on the aerosol properties and the chemistry of the lower stratosphere f) the nature of air motions in the lower stratosphere as revealed by variations in aerosol abundance.

Summary of Progress and Results

The reliability and accuracy of the FCAS were improved following the implementation of a pulse height analysis and data storage system designed at the University of Denver. The FCAS and CNC II were moved from spearpods to superpods on the ER-2 in 1996. Aerosol measurements were made from the ER-2 in 1994 ASHOE/MAESA, and in 1995 and 1996 in STRAT. These measurements covered latitude ranges from ~60°N to ~65°S and were made at altitudes from ~9 to

~20 km. These and previously acquired data, as well as analyses, have contributed to several investigations.

- We have characterized the evolution of the aerosol resulting from the eruption of Mt. Pinatubo. It was shown that the transport of tropospheric air into the lower stratosphere was important in the clean up of the Pinatubo aerosol.
- Analysis of ER-2 measurements of aerosol, nitrogen species, chlorine and hydrogen radicals demonstrated the importance of heterogeneous chemistry in determining the partitioning of the nitrogen, chlorine and hydrogen species in the lower stratosphere and permitted quantitative predictions to be successfully tested.
- Measurements of volatile and nonvolatile condensation nuclei in the plume emitted by a Concorde supersonic aircraft permitted us to conclude that fuel sulfur was converted very rapidly to small sulfuric acid particles. This result was unexpected. Based on these measurements, we concluded that a fleet of aircraft operating in the lower stratosphere could cause a doubling of aerosol surface area in the region. The rapid conversion of the fuel sulfur to particles is important in determining the size of the perturbation.
- Analysis of tropical and extratropical profiles of condensation nuclei permitted us to conclude that particles produced in the tropical, upper troposphere serve as a source for the stratospheric aerosol and that transport and coagulation of these particles explains the observed number concentration in the stratosphere.
- The formation of one Antarctic polar stratospheric cloud was shown to be consistent with the formation of a super-cooled ternary solution of sulfuric acid, nitric acid and water.

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E. Rocket-Borne Measurements

Rocket-Borne Temperature and Wind Measurements

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Research Objectives

Rocket-borne instrumentation provides *in situ* temperature and wind measurements for the verification of NASA satellite remotely sensed temperature and wind data. Rocket measurements are supported with balloon-borne instrumentation, which along with the rocket measurements provide complete profiles from the Earth's surface to the upper levels of the rocket measurement. New algorithms and enhanced error analysis studies have improved the quality, accuracy, and reliability of the measurements provided. Observations from Wallops Island, Norway, Sweden, and Brazil have provided NASA researchers with ground-truth data to allow verification of their remote measurements and which allows atmospheric chemists to better define the distribution of constituent data. Other national and international investigators also benefit from the rocket-borne measurements. This program is synergistic in that it allows interaction between remote and *in situ* measurement investigators.

Summary of Progress and Results

Rocket-borne instrumentation provides primarily temperature and wind measurements between ~18 km to the upper limit of the rocketsonde measurement, 65 km for *in situ* temperature sensing and 90 km for the inflatable falling sphere. Satellite remote sensing instruments need ground-truth data (i.e., correlative *in situ* measurements) for validation of the instruments. During the period of FY 1994 through FY 1996 rocket-borne instruments have provide verification for the instruments on the Upper Atmosphere Research Satellite (UARS). The UARS instruments utilizing the rocketsonde data have been the High Resolution Doppler Interferometer (HRDI), Wind Interferometer Instrument (WINDII), Improved Stratospheric and Mesospheric Sounder (ISAMS), Halogen Occultation Experiment (HALOE), and the comparison of temperature data between rocketsondes and the Limb Infrared Monitor of the Stratosphere (LIMS) located on the Nimbus 7 satellite was revisited.

The recent application of rocket data has been with data from HRDI which suggests relatively good agreement. As part of this study a new wind reduction algorithm was developed at Wallops which allows improved vertical resolution of wind profiles at altitudes above 70 km. Request for rocketsonde data for various purposes, such as satellite remote sensor validation, lidar validation, and for atmospheric structure studies are often received making the rocket measurement program a valuable adjunct to upper atmospheric research. Improved measurements, especially those concerning temperature accuracy are necessary and important data for the use of scientists and atmospheric chemists involved with study of constituent distributions and interaction. Temperature accuracy of better than 1°C is usually critical for constituent analysis.

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Rocket-Borne Cryogenic Whole Air Sampler

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Research Objectives

The Cryogenic Whole Air Sampler payload [CWAS] was developed to provide accurate mixing ratio for CH_4, CO, CO_2, N_2O and a variety of fluorocarbon species as part of NASA's Correlative Measurements Program in support of the Upper Atmosphere Research Satellite. Precise isotope measurements [dO17 and dO18] for CO_2, N_2O and O_2 were also obtained as part of a study of chemical reactions with mass independent fractionation.

Summary of Progress and Results

The CWAS payload was successfully launched eighteen times from WSMR in coordination with UARS overflights and provided mixing ratio data for HALOE, CLAES and ISAMS from 30 to 60 km. The samples were analyzed using the laboratory facilities of the University of Pittsburgh [MR] and the University of California (San Diego) [isotope studies]. The results of the validation comparisons were quite successful and are discussed below. The isotope measurements have discovered an unsuspected link between ozone and CO_2 chemistry; the results were published in a recent Science report.

Publications

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LABORATORY STUDIES

A. REACTION KINETICS AND PHOTOCHEMISTRY
B. SPECTROSCOPY

A. Reaction Kinetics and Photochemistry

Kinetics and Mechanisms of the Atmospheric Photooxidation of Some Hydrochlorofluorocarbons and Hydrofluorocarbons

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Research Objectives

Laboratory investigations of the kinetics and mechanisms of the atmospheric oxidation of some compounds that are replacements for the ozone-depleting chlorofluoromethanes are being conducted. These alternatives are already in use, or are intended for use, in large-scale technological applications such as refrigeration, and as polymer foam blowing agents. They are partially halogenated low molecular weight hydrocarbons possessing at least one C-H bond. Reaction with hydroxyl radicals in the troposphere initiates free radical oxidative degradation reactions that produce halogenated final products. It is important to understand the atmospheric chemistry of these compounds to determine the full impact of using them on a global scale. We are using flash photolysis with time-resolved mass spectrometry for laboratory studies of the kinetics and mechanisms of the relevant elementary chemical reactions. The research seeks to assess the importance of various reaction pathways and the ultimate environmental sinks for the chlorine and fluorine.

Summary of Progress and Results

The replacements for the chlorofluoromethanes (CFCs) are hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). Reaction with OH radicals produces halogenated alkyl radicals which rapidly react with O_2 to form haloalkylperoxy radicals. An important atmospheric reaction of the peroxy radicals is with NO to form NO_2 and the corresponding haloalkoxy radical. The oxy radical is a key intermediate in the oxidative degradation chain. In our work over the past two years, we have designed experiments for generation of halogenated alkyl radicals by flash photolysis. With appropriate partial pressures of O_2 and NO in the reaction mixture, the peroxy radicals are formed on a time scale of microseconds, and their kinetic decay by reaction with NO occurs on a millisecond time scale. We have used this method to study the kinetics of several peroxy radicals with NO. We have also been able to gain information on the atmospheric fate of the oxy radicals formed from each of these peroxy radicals. The replacement compounds that we have investigated thus far are CH_2FCl (HCFC-31), $CFCl_2CH_3$ (HCFC-141b), CF_3CFH_2 (HFC-134a), and CF_3CFClH (HCFC-124).

We have determined the kinetics of NO with CF_3O_2, $CHFClO_2$, $CFCl_2CH_2O_2$, CH_3CFClO_2, CF_3CFClO_2 and CF_3CFHO_2. The 298 K rate coefficients are all in the range 1.3 to 1.9 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, larger than the reported values for CH_3O_2 + NO and $CH_3CH_2O_2$ + NO by

approximately a factor of two or slightly more. The temperature dependence of the $CFCl_2CH_2O_2$, CH_3CFClO_2, CF_3CFClO_2 radical reactions with NO have negative temperature dependencies that can be expressed as $k = k_{298}[T/298]^{-n}$, where n is about a factor of 1.5 to 2 greater than for CH_3O_2 and $CH_3CH_2O_2$. The electronegative halogen substituents have a measurable effect on the energetics of the peroxy radical-NO interaction. This might be describable as an inductive effect, weakening the O-O bond.

The various oxy radicals that are formed by the peroxy + NO reactions have widely differing behavior. Some halogen substitutional patterns cause bond weakening to the extent that unimolecular dissociation occurs at temperatures lower than 298 K. For example, the CF_3CFHO radical dissociates by C-C bond scission on a time scale of milliseconds or shorter. When there is a Cl atom in the a-position, rapid unimolecular elimination of Cl can occur. We have found this to be the case for CH_3CFClO, CF_3CFClO, and CHClFO. The CF_3O radical does not dissociate in our experiments. However, it does react with NO, and we have measured the 298 K rate coefficient for that reaction. There has been a question whether CF_3O can participate in an O_3 removal cycle. The rate coefficient we found is sufficiently large that CF_3O cannot be involved in such a cycle, in agreement with recent results from other laboratories. The $CFCl_2CH_2O$ radical does not undergo unimolecular decomposition, but does react with O_2 to form HO_2 and $CFCl_2C(O)H$. We have been able to investigate the kinetics of this reaction by direct mass spectrometric observation of the rate of formation and decay of the oxy radical.

We have also been able to measure the kinetics of the reactions of Cl and ClO with each of the radicals $CFCl_2CH_2O_2$ and CH_3CFClO_2. These are reactions that will occur in the stratosphere, since the ozone depletion potential of HCFC-141b is about 0.1, and both peroxy radicals would be formed following transport of this substance into the stratosphere. However, the rate coefficients are too small for these reactions to compete effectively with NO for these radicals.

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Atmospheric Photochemical Kinetics

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Research Objectives

To conduct laboratory studies of stratospheric photochemistry, including absorption cross sections, photolysis quantum yields, product distributions, and reaction rate constants.

Summary of Progress and Results

A method has been developed for the measurement of OH rate constant ratios for reactions of HFCs, HCFCs, and fluoroethers. Using the database of approximately thirty-five rate constants generated by these measurements, a technique for accurate and efficient estimation of OH abstraction rate constants has been developed.

Studies of the ClO dimer, ClOOCl, have led to new and lower photochemical cross sections of that intermediate.

Publications

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Reaction Intermediates and Mechanisms

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Research Objectives

This task is aimed at the elucidation of the kinetics, product distributions, and mechanisms of reactions relevant to stratospheric and tropospheric chemistry. Primary emphasis is placed on processes that function as rate limiting steps in catalytic ozone destruction cycles or that impact the partitioning within chemical families (e.g., ClO_x, BrO_x, FO_x, NO_x, and HO_x). Data is obtained using laboratory based chemical reactors. The laboratory techniques employed include discharge flow - mass spectrometry, laser photolysis - laser induced fluorescence, and discharge flow - Fourier transform spectroscopy.

Summary of Progress and Results

Our research activities over the past three years have been directed towards providing reaction rate and photochemical yield information for assessments of the potential ozone impacts of several anthropogenic emissions, namely, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (e.g., HCFC 134a), and aircraft exhaust. Substantial progress has been made in all areas as detailed below:

- A firm qualitative connection between anthropogenic chlorofluorocarbon emissions and global ozone depletion has been developed over the last several years. However, many important quantitative questions remain, especially as regards observed polar ozone loss. We have been investigating the possible existence of additional chlorine reservoir species through low temperature studies of chlorine-containing reaction systems. Following our discovery of the novel compound choryl nitrate, we have succeeded in obtaining structural information for the higher oxide, Cl_2O_3, through submillimeter spectroscopic interrogations of Cl + OClO reaction mixtures. The spectroscopic data has enabled investigators to determine the thermochemical stability of the compound over a range of atmospheric temperatures.
- Atomic fluorine, a primary photodecomposition product of HCFC 134a, is rapidly converted to FO_2 in the atmosphere. In order to assess the importance of FO_2 in stratospheric ozone chemistry, we have studied the kinetics of the reactions $FO_2 + NO$ and $FO_2 + NO_2$ as functions of temperature at 1 Torr total pressure using a discharge-flow mass spectrometric technique. The observed temperature dependencies of the rate coefficients indicate that the reactions occur primarily by simple bimolecular, rather than termolecular, mechanisms. Mass spectral product

studies are consistent with bimolecular processes involving F atom extraction from FO_2. Upper limits for the rate coefficients of $FO_2 + O_3$, $FO_2 + CH_4$, and $FO_2 + C_2H_6$ have also been determined with the same experimental system at room temperature. As part of the $FO_2 + O_3$ study, an investigation of the reaction $FO + O_3$ was conducted. The results of these studies reveal that a catalytic ozone removal cycle involving FO and FO_2 is ineffective relative to various FO_x removal processes.

- The steady rise of subsonic air travel and proposals for development of supersonic aircraft have led to concern over the effects of their emissions on the atmosphere. In support of assessments of aircraft impacts, we have been examining chemical interactions between nitrogen oxides and hydrocarbons which may moderate the effect of aircraft NO_x emissions on ozone. In particular, we have studied the chemistry of HO_2NO_2 (PNA) and $CH_3CO_3NO_2$ (PAN), species which have drawn attention because of noted discrepancies between measured and modeled values of the NO_x/NO_y ratio in the upper troposphere and lower stratosphere.

In one set of experiments we studied the interaction of PNA with solid H_2O-ice. A coefficient of 0.15 was measured for the uptake of PNA on ice, however, the process was found not to result in the production of gas phase products. Studies of the condensed phase products suggest that PNA, like HNO_3, tends to be hydrated in the presence of water. These observations suggest a potential atmospheric role for PNA heterogeneous chemistry on cirrus or polar stratospheric clouds.

In another set of investigations, PAN vapor was photolyzed at 248 nm and the NO_2 photoproduct was detected by laser induced fluorescence at 511 nm. The quantum yield for the production of NO_2 was determined by comparison to HNO_3 photolysis data taken under identical experimental conditions. The average of data collected over a range of total pressures, precursor concentrations, and buffer gases was 0.83 for the NO_2 quantum yield, with a statistical uncertainty (two standard deviations) of 0.09. This result, when combined with our very recent data on the NO_3 quantum yield, indicates that NO_2 and NO_3 represent the sole nitrogen containing products of 248 nm photolysis of PAN.

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Chemical Kinetics of the Stratosphere

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Research Objectives

To determine rate constants and product yields of atmospheric reactions by using laboratory kinetics and photochemical techniques; to develop new experimental methods to detect reactive species under conditions occurring in the atmosphere; and to study the physical-chemical properties of atmospheric aerosol surfaces.

Summary of Progress and Results

Reaction probabilities of $ClONO_2 + H_2O$, $ClONO_2 + HCl$, and $HOCl + HCl$ were measured on liquid sulfuric acid surfaces. The results show that all these reactions depend markedly on temperature at a fixed H_2O partial pressure: they proceed efficiently at temperatures near 200 K and much slower at temperatures near 220 K.

Freezing points were determined for $H_2SO_4 \cdot H_2O$ (SAM) and $H_2SO_4 \cdot 3H_2O$ (SAT) and the solids were characterized by using BET adsorption. It was found that SAM crystallizes readily at temperatures between 220 and 240 K. Reaction probability measurements indicate that the hydrolysis of N_2O_5 and $ClONO_2$ are significantly suppressed on SAM surfaces.

The hydrolysis of N_2O_5 and $ClONO_2$ were also investigated on $H_2SO_4/HNO_3/H_2O$ ternary solutions to determine the effect of HNO_3. The reaction probability for N_2O_5 hydrolysis was near 0.1 and independent of temperature in HNO_3 free solutions; in the presence of HNO_3 the reaction probability decreased to about 0.02 at 195 K. On the other hand, the hydrolysis of $ClONO_2$ on liquid H_2SO_4 was not affected by the presence of HNO_3.

A new mechanism for chlorine activation involving the reaction of HCl with HONO on liquid H_2SO_4 was investigated. The measured uptake coefficient of HONO in H_2SO_4 increases with increasing acid content. In solutions greater than 70 wt% H_2SO_4, HONO undergoes irreversible reaction with an uptake coefficient of about 0.07. HCl reacts with HONO dissolved in H_2SO_4 with $a = 0.01 - 0.02$, releasing gaseous ClNO.

The reactions, (1) $HNO_3 + NaCl \rightarrow HCl + NaNO_3$ and (2) $N_2O_5 + NaCl \rightarrow ClNO_2 + NaNO_3$ have been investigated over the temperature range 223 to 296 K. For dry NaCl the reaction probability

$\gamma(1) = 0.013$ at 296 K and > 0.008 at 223 K. HCl was found to be the sole gas-phase product of this reaction. The mechanism changed from heterogeneous reaction to mostly physical adsorption when the NaCl was cooled from 296 to 223 K. For reaction 2 with dry NaCl, $\gamma(2) = 1 \times 10^{-4}$ at both temperatures studied. The gas-phase reaction product was found to be $ClNO_2$. An enhancement in reaction probability was observed if water is not completely removed.

In the work described above, a constant surface reactivity or uptake probability was assumed. This is not always the case since the surface can be modified by adsorption and by product formation. An example of this is the reaction of HNO_3 with NaCl at 223 K. The observed uptake probability changes rapidly and over a few minutes the surface becomes equilibrated or deactivated. When HNO_3 is no longer added to the gas stream, HNO_3 desorbs almost quantitatively from the NaCl surface; this implies that the observed deactivation is due to physical adsorption. Numerical methods have been used to model the deactivation in porous solids and obtain rate coefficients for adsorption, desorption and surface reaction.

The morphology of thin ice films formed by deposition from the vapor phase has been studied by using environmental scanning electron microscopy. Surface areas were determined from the BET analysis of gas adsorption isotherms. The results for ices prepared at 196 K and 77 K are consistent with previous data obtained by using thicker ice films prepared in a separate apparatus. The uptake of HCl in ice films prepared at 196 K using the same flow-tube reactor was found to be $\sim 1 \times 10^{14}$ molecules/cm^2 when a partial pressure of HCl near 5×10^{-7} Torr was used.

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Photochemical and Kinetic Measurements of Stratospheric and Tropospheric Importance

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Research Objectives

This task focuses on the elucidation of stratospheric photochemical processes through laboratory studies of select chemical reaction systems. Experiments are designed and conducted to determine the temperature and pressure dependencies of rate constants and to infer the mechanisms for those processes important in the modeling of atmospheric chemistry. Photochemical parameters are also determined to assist in the kinetic measurements or to aid in the interpretation of the data. While the research emphasis is directed towards an assessment of the effects of anthropogenic activity on stratospheric chemical composition, certain predominantly tropospheric reaction systems are also investigated because of their influence on chemical transport to the stratosphere and/or their mechanistic similarities to stratospheric processes.

Under this task, the principal investigator also serves as a member of the NASA Panel for Data Evaluation and assists in the annual preparation of a tabulation of evaluated kinetic and photochemical data applicable to atmospheric modeling. He also provides advisory services to the Upper Atmosphere Research Program (UARP) of NASA's Mission to Planet Earth (MTPE) regarding the direction, evaluation, and review of the major program elements. Finally, the PI participates as an author and reviewer in various national and international assessment activities relating to atmospheric chemistry in general and stratospheric ozone in particular.

Summary of Progress and Results

Laboratory activities under this task during the period 1994 through 1996 fall into two categories: (i) hydroxyl radical kinetic investigations performed using the flash photolysis resonance fluorescence (FPRF) technique; and (ii) free radical photochemistry and kinetics studied using pulsed excimer laser photolysis (for radical generation) coupled with UV absorption spectroscopy (for kinetic analysis), the LPAS (or laser photolysis absorption spectroscopy) technique. Accomplishments include:

FPRF: The temperature dependencies of the rate constants for the reactions of OH radicals with a variety of possible chlorofluorocarbon (CFC) replacement compounds and other atmospheric

source gases have been measured. Studies have included the following hydrofluorocarbons: CH_3CF_3 (HFC-143a), $CHF_2CH_2CF_3$ (HFC-245fa), $CHF_2CF_2CH_2F$ (HFC-245ca), $CF_3CHFCHF_2$ (HFC-236ea), CF_3CHFCF_3 (HFC-227ea), and $CF_3CH_2CH_2CF_3$ (HFC-356ffa) as well as CH_2ClBr, a naturally occurring halogen source gas that is also an effective industrial cleaning agent and fire suppressant. The rate constant results thus obtained were used in a comparative kinetic analysis with those for methyl chloroform to determine approximate tropospheric lifetimes of the compounds. For CH_2ClBr, measurements were also made of the UV spectra between 187 to 290 nm and of the water solubility in an effort to better define the total atmospheric lifetime of this compound for use in determining its ozone depletion potential.

Similar kinetic studies were conducted with dimethyl carbonate ($CH_3O(CO)OCH_3$), a potential automotive fuel. In this case, the OH reaction kinetics used (together with detailed mechanistic information obtained by researchers at the Ford Motor Company Research Laboratory) in a modeling analysis to establish the compounds' atmospheric reactivity with respect to tropospheric ozone formation.

LPAS: Laser photolytic production of IO (from $N_2O/I_2/N_2$ mixtures) and BrO (from $N_2O/Br_2/N_2$ mixtures) was used to investigate atom and radical kinetics in the individual and mixed systems. Room temperature rate constants were thus obtained for the reactions O + I_2, O + IO, IO + IO, O + Br_2, O + BrO, BrO + BrO, I + BrO, and BrO + IO. These results allow for a more quantitative determination of the role of iodine chemistry in lower stratospheric ozone loss. Absorption cross-section measurements of IO between 340 to 450 nm revealed two new absorption peaks, resulting in a much shorter calculated photolytic lifetime for IO in the troposphere than earlier published values. A BrO cross section at 338.5 nm determined in these studies is in excellent agreement with earlier workers.

Assessments and Reviews: During the three year period covered by this report, the PI participated in the preparation and review of the 11th Evaluation of Photochemical and Kinetic Data for Use in Stratospheric Modeling by the NASA Panel for Data Evaluation. He also participated in the preparation of NASA's 1993 Triennial Report to the Congress and the Environmental Protection Agency on our present state of understanding of the upper atmosphere (stratosphere) as mandated by the Clean Air Act Amendments. Finally, the PI co-authored a chapter on the atmospheric chemistry of methyl bromide in the 1994 international scientific assessment of ozone depletion. This assessment was coordinated by the World Meteorological Organization and the United Nations Environment Programme as prescribed under the provisions of the Montreal Protocol on Substances that Deplete the Ozone Layer.

More detailed information on all of the activities that have been described above may be found in the following publications.

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Homogeneous and Heterogeneous Processes of Atmospheric Interest

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Research Objectives

The primary objective of this task is to obtain direct laboratory measurements of kinetic rate parameters for homogeneous and heterogeneous reactions important in stratospheric chemistry, and to develop new experimental techniques for the laboratory study of polar ozone chemistry.

Summary of Progress and Results

Laboratory activities under this task during 1995 and 1996 concern the heterogeneous chemistry on the surface of stratospheric aerosols.

Accomplishments include:

- *Hydrolysis of N_2O_5 and $ClONO_2$ on the $H_2SO_4/HNO_3/H_2O$ ternary solutions:* The reaction probabilities of N_2O_5 and $ClONO_2$ with H_2O on liquid sulfuric acid surfaces have been re-examined to survey the effect of HNO_3 on these two hydrolysis rates, using a fast flow reactor coupled to a chemical ionization mass spectrometer. The measurements were carried out by maintaining constant H_2O and HNO_3 partial pressures and by varying temperatures between 227 and 195 K in order to mimic compositions representative of stratospheric aerosols. For experiments excluding HNO_3, the reaction probability of N_2O_5 hydrolysis was found to be near 0.1, independent of temperature and H_2SO_4 content. This is in agreement with results previously measured under similar conditions. In the presence of gaseous HNO_3 at stratospheric concentrations, the reaction probability was observed to decrease from about 0.09 at 218 K to about 0.02 to 0.03 at 195 K for $PH_2O = 3.8x10^{-4}$ - $1.0x10^{-3}$ Torr, showing that incorporation of HNO_3 into liquid sulfuric acid greatly retarded the N_2O_5 hydrolysis. The $ClONO_2$ reaction with H_2O on liquid sulfuric acid, on the other hand, did not appear to be affected by the presence of HNO_3.
- *Sulfuric acid monohydrate:* We have investigated some thermodynamic properties (i.e., freezing/melting points) and heterogeneous chemistry of sulfuric acid monohydrate (SAM, H_2SO_4ïH_2O), using a fast flow-reactor coupled to a quadrupole mass spectrometer. The freezing point observations show that for sulfuric acid contents between 75 and 85 wt% the

monohydrate crystallizes readily at temperatures between 220 and 240 K. Once formed, SAM can be thermodynamically stable in the H_2O partial pressure range of (1-4)x10^{-4} Torr and in the temperature range of 220 to 240 K. For a given H_2O partial pressure, SAM melts at lower temperatures. The reaction probability measurements indicate that the hydrolysis of N_2O_5 is significantly suppressed due to the formation of crystalline SAM: the reaction probability on water-rich SAM is on the order of 10^{-3} at 210 K and decreases by more than an order of magnitude for the acid-rich form. The hydrolysis rate of $ClONO_2$ on water-rich SAM is even smaller, on the order of 10^{-4} at 195 K. No enhancement of these reactions is observed in the presence of HCl vapor at the stratospheric concentrations. In addition, BET analysis of gas-adsorption isotherms has been performed to characterize the surface roughness and porosities of the SAM substrates. The results suggest the possible formation of SAM in some regions of mid- or low latitude stratosphere and, consequently, much slower heterogeneous reactions on these frozen aerosols.

- *Heterogeneous chemistry of HO_2NO_2 on liquid sulfuric acid:* The interaction of HO_2NO_2 (peroxynitric acid, PNA) vapor with liquid sulfuric acid surfaces was investigated for the acid contents ranging from 50 to 70 wt% and over a temperature range from 205 to 230 K, using a fast flow-reactor coupled to a chemical ionization mass spectrometer. PNA was observed to be physically taken up by liquid sulfuric acid, without undergoing irreversible aqueous phase reactions. The uptake coefficient was measured to vary from about 0.2 on 55 wt% H_2SO_4 to 0.06 on 70 wt% acid solution. From the time-dependent uptake, the quantity H(Dl)1/2 (that is, the product of the Henry's law coefficient and the square root of the liquid-phase diffusion coefficient) was obtained. Henry's law solubility coefficient of PNA in liquid sulfuric acid was then derived by estimating the liquid-phase diffusion coefficient based on a cubic cell model. In general, the solubility was found to increase with decreasing acid content and decreasing temperature. For a constant H_2O partial pressure of 6.1 x 10^{-4} Torr, H was determined to be about 106 M atm^{-1} at 204 K and 105 M atm^{-1} at 223 K, as the acid content was varied from 55 to 70 wt%. Potential heterogeneous reactions involving PNA on liquid sulfuric acid were also examined. The measured solubilities reveal that peroxynitric acid should exist predominately in the gas phase under conditions characteristic of mid-or lower latitude stratosphere. For winter polar stratospheric conditions, however, incorporation of PNA into sulfate aerosols may lead to significant redistribution of PNA from the gas to condensed phases, thus affecting stratospheric HO_x and NO_x concentrations.
- *Heterogeneous chemistry of HONO on liquid sulfuric acid:* Heterogeneous chemistry of nitrous acid HONO on liquid sulfuric acid H_2SO_4 was investigated at conditions that prevail in the stratosphere. The measured uptake coefficient of HONO on H_2SO_4 increased with increasing acid content, ranging from 0.03 for 65 wt% to about 0.1 for 74 wt%. In the aqueous phase, HONO underwent irreversible reaction with H_2SO_4 to form nitrosyl sulfuric acid NO+HSO_{4-}. At temperatures below 230 K, NO+HSO_{4-} was observed to be stable and accumulated in concentrated solutions (> 70 wt % H_2SO_4), but was unstable and quickly re-generated HONO in dilute solutions (< 70 wt%). HCl reacted with HONO dissolved in sulfuric acid, releasing gaseous nitrosyl chloride (ClNO). The reaction probability between HCl and HONO varied from 0.01 to 0.02 for 60 to 72 wt% H_2SO_4. In the stratosphere, ClNO photodissociates rapidly to yield atomic chlorine, which catalytically destroys ozone. Analysis of the laboratory data reveals that the reaction of HCl with HONO on sulfate aerosols can affect stratospheric ozone balance during elevated sulfuric acid loading after volcanic eruptions or due

to emissions from the projected High-Speed Civil Transport (HSCT). The present results may have important implications on the assessment of environmental acceptability of HSCT.

- *Mechanism for Type I PSCs formation:* Results of laboratory simulations of the growth of nitric acid trihydrate, $HNO_3 \cdot 3H_2O$, on sulfuric acid tetrahydrate, $H_2SO_4 \cdot 4H_2O$, are presented. The observations reveal that under typical stratospheric conditions uptake of HNO_3 on a $H_2SO_4 \cdot 4H_2O$ substrate results in a surface coverage of approximately one monolayer or less, and that initial $HNO_3 \cdot 3H_2O$ nucleation requires a large supersaturation. We also observe that a $H_2SO_4 \cdot 4H_2O$ substrate, onto which a $HNO_3 \cdot 3H_2O$ film has been deposited and subsequently evaporated, exhibits a remarkable enhancement in its nucleation ability for this nitric acid hydrate. In the stratosphere, PSC particles may experience repeated cycles of evaporation and condensation of HNO_3 on preexisting background frozen sulfate aerosols. Hence, growth of $HNO_3 \cdot 3H_2O$ on preactivated aerosols provides one important mechanism for polar stratospheric cloud formation and denitrification.

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Laboratory Studies of Nitric Acid Hydrate Aerosols: Formation and Characterization

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Research Objectives

Stratospheric aerosols are now known to be important to a wide variety of atmospheric processes, including ozone depletion and global warming. Although a great deal of laboratory work has been carried out on thin films of the ices mentioned above, there is a need to develop new approaches for obtaining detailed information on the formation of stratospheric aerosol species, as well as the characterization of their properties under conditions that, as closely as possible, mimic those found in the stratosphere. A new approach has been developed in our laboratory for obtaining frequency dependent optical constants directly from the infrared spectroscopy of aerosols. A number of interesting cases have and are being explored which amply demonstrate the power of the method. In several cases, the results obtained from the aerosol method are quite different from those obtained from thin films. Although the cause of this is still not well understood (it may be due to the fact that the film studies can suffer from substrate interference), the results do illustrate the necessity for alternative approaches for studying these systems. We have also used the infrared studies to explore phase transitions in isolated particles.

Summary of Progress and Results

We have used a low-temperature flow cell and broad band FT-IR spectroscopy to study a variety of aerosol systems. Perhaps the most important feature of this cell is that it is comprised of four regions, each of which can be independently temperature controlled. We have used this feature to form aerosols, control their size, and either heat or cool them to their final observation temperature. Aerosols are formed in the cell by flowing gases of interest into the top of the cell with a buffer gas of either helium or nitrogen. As the gas cools in the cell, it becomes supersaturated and an aerosol forms. By controlling the temperature of the region in which the aerosol forms, we can easily generate aerosols with radii from < 0.1 mm to > 1.0 mm. For systems with extremely low vapor pressures, like sulfuric acid, we use bubblers and more recently vaporizers, to generate the aerosols upstream of the cell.

As a test of our new method for determining refractive index data for these aerosols we began with water ice. The basis of the method is that the non-scattering aerosol (small particle) spectrum is sensitive (to first order) only to the imaginary part of the refractive index (absorption). This is an approximation that needs to be corrected for later, but serves as a good starting point. Within this approximation, therefore, this spectrum provides us with a measure of the frequency dependent imaginary refractive index. The only thing we do not know is the absolute scaling factor, since this is related to the number density of the aerosols in the cell. In a thin-film experiment, the thickness of the sample is measured to provide the analogous data. For aerosols, this is difficult, and as it turns out, unnecessary. Indeed, we can take advantage of the fact that the scattering aerosol is sensitive to both the real and the imaginary components to obtain the scaling factor for the latter. If we calculate the scattering spectrum from Mie theory, using an improperly scaled imaginary set of refractive index data to generate the real part using a Kramers-Kronig method, we will get the wrong relative magnitudes of the scattering and absorption features in the spectrum. As a result, this can be used in an iterative procedure to fit the scattering data to determine the scaling factor. Second order corrections are applied to correct for the earlier assumptions, but the method converges rather well to results that agree with the literature values, where available.

We have found that the temperature dependence of the optical constants of ice is very strong, suggesting that it must be accounted for an could have very important implications in modeling [Clapp *et al.*, 1995]. Given this, we are continuing studies of other water-rich ices as a function of temperature, including binary and ternary mixes with nitric and sulfuric acids.

The above method has been used to generate refractive indices for NAT at 175 K [Richwine *et al.*, 1995] and work is presently progressing on the temperature dependence of the optical constants of NAT and NAD, as well as that of sulfuric acid at various compositions. In the latter case, the problem of aerosol composition determination needs to be addressed. We have done this in two ways. First, we used the area method of Tolbert and coworkers [Anthony *et al.*, 1995] to determine composition of sulfuric acid/water aerosols observed over a broad range of temperatures. This method is empirical and is expected to provide only an estimate at best. In our other approach, we use the fact that the aerosol composition can be determined by measuring the vapor pressures of the aerosol components. This method relies on the assumption that the vapor phase is in equilibrium with the aerosol. We measured the water vapor intensities in the FT-IR spectrum and fit them with the aid of the HITRAN 1992 database. The fit yielded a value of the water vapor pressure that was subsequently used in the model of Carslaw, *et al.* [1995] in order to derive the aerosol composition. Due to the limited sensitivity of the FT-IR method, this only worked at high temperatures and dilute compositions where the water vapor pressure was high. The two methods are consistent over the temperature range in which the latter is viable. This fact confirms that the vapor is in equilibrium with the aerosols, as expected. Work proposed for the next grant period will extend the useful range of the vapor pressure method by employing a tunable diode laser system that will be able to measure very low vapor pressures.

We have also observed changes in the spectral bands of sulfuric acid aerosols that provide information on the freezing of these particles under stratospheric conditions. The results clearly show that even when ice nucleates in these particles, they do not immediately freeze, as had been assumed previously [Jensen *et al.*, 1991; Luo *et al.*, 1992, 1994]. These results agree with recent observations of dilute sulfuric acid/water aerosols by Bertram, *et al.* [1996]. On the time scales of our experiments (minutes) the entire particle is only observed to freeze at temperatures well below

those encountered in the stratosphere. Future experiments will need to test these results at longer times.

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Laboratory Chemistry of Halogen Compounds Related to Stratospheric Ozone Depletion

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Research Objectives

This task is aimed at characterizing in the laboratory chemical processes which are potentially important in the stratosphere in connection with ozone depletion. The studies involve homogeneous gas phase reactions, with measurements of elementary rate constants and photochemical parameters over pressure and temperature ranges which cover lower stratospheric conditions. The systems under study include reactions of the HO_2, ClO and BrO radicals.

Summary of Progress and Results

The turbulent flow technique has been utilized for elementary rate constant measurements of chlorine atom reactions with nitrogen dioxide, methane and ozone, using resonance fluorescence in the VUV to monitor the chlorine atoms; the results are in very good agreement with earlier literature values obtained using different techniques. The reactions of the HO_2 radical with BrO and with NO were also investigated using the turbulent flow approach, coupled in this case to chemical ionization mass spectrometry (CIMS) for the detection of reactants and products. These are the first set of direct measurements for these reaction rate constants carried out at moderate pressures.

Using the same turbulent flow - CIMS technique, the OH + ClO reaction has been investigated, placing special emphasis on the channel producing $HCl + O_2$, which is potentially important in the stratosphere. The overall rate constant measured at 298 K and 100 Torr total pressure is in good agreement with the accepted literature value. The results indicate that the predominant channel is the one yielding HO_2 and Cl; production of HCl was directly verified, with a branching ratio, however, of at most a few percent under those temperature and pressure conditions.

The quantum yields for the photodecomposition of $ClONO_2$ and Cl_2O have been determined at wavelengths of around 300 to 330 nm and at pressures of a few hundred Torr. The results indicate unit quantum yield for photolysis; no indication of long-lived intermediates was found under those experimental conditions.

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Molecular Beam Studies of Stratospheric Photochemistry

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Research Objectives

The objective of this laboratory task is to investigate the photochemistry of chlorine-containing species of relevance to stratospheric chemistry. Our goal is to identify the photofragments formed from ultraviolet photolysis of these compounds and to determine the relative product yields. Our approach, photofragment translational spectroscopy, takes advantage of the collisionless conditions in molecular beams to detect the primary products in the absence of secondary collisions. Such experiments can lead to accurate photofragment branching ratios as well as measurements of photodissociation dynamics, e.g., product translational energy release. A central target of these studies is chlorine peroxide, ClOOCl, which is a predominant form of chlorine in the perturbed polar stratosphere. In current models, the photolysis of ClOOCl is a major pathway leading to polar ozone depletion. The current experiments were conceived to provide an independent measure of the ClOOCl photolysis branching ratio using a technique which complements flow tube methods. A critical technological goal has been the development and testing of a novel photolysis source for generating a sufficiently intense molecular beam of chlorine peroxide. Although such a source is not pure, our ability to measure product dynamics allows us to distinguish photofragment signals from different channels and different precursors. A second goal is to study the long wavelength photolysis of $ClONO_2$. Specifically, we seek evidence for a proposed long-lived state which, if formed in high yields, could alter the quantum yield for $ClONO_2$ photolysis in the stratosphere and hence change predicted chlorine budgets.

Summary of Progress and Results

- *Photolysis of Chlorine Nitrate.* We have completed studies on the photodissociation of chlorine nitrate, $ClONO_2$, one of the major chlorine reservoirs in the stratosphere. Most of our effort in the current period has been directed towards investigating the photolysis of $ClONO_2$ at 308 nm. These studies complement our earlier work at shorter wavelengths (193 and 248 nm), which demonstrated the significance of the $ClO + NO_2$ channel, in addition to the $Cl + NO_3$ channel. The new study at 308 nm is in a region of more significance for lower stratospheric photochemistry, although still somewhat to the blue of the peak in the wavelength dependence

of the photodissociation rate *J*. We find that two channels are important, ClO + NO_2 and Cl + NO_3, with a branching ratio of 0.33:0.67 at 308 nm. This branching ratio is similar to that at 193 nm and slightly smaller than that at 248 nm. We also place an upper bound on the relative yield for a long-lived state of < 0.07. Finally, we completed the analysis and write-up of data taken earlier on the photolysis at 193 and 248 nm. These results are consistent with recent flow tube studies. They also indicate that O atoms are produced as secondary fragments from decomposition of primary NO_3 fragments.

- *Dichlorine monoxide.* Cl_2O is the precursor in our proposed ClOOCl experiment. As a first step, we have investigated the photodissociation of Cl_2O at 308, 248, and 193 nm. Early in the current performance period, we followed through on the analysis and write-up of data taken on experiments performed earlier. We find rapid dissociation to ClO + Cl products at all wavelengths, and we have measured the product translational and angular distributions. In addition, at 193 nm we observe an unquantified yield of the channel Cl_2 + O, with much of the Cl_2 dissociating to 2Cl. The distributions measured at 308 nm are essential for subtracting Cl_2O contributions to the photofragment signal observed in our ClOOCl experiment.

- *Chlorine Peroxide.* We have developed and tested a novel molecular beam source of ClOOCl. Our first experiments on the photodissociation of chlorine peroxide at 308 nm are currently underway.

  The molecular beam of ClOOCl is generated by photolysis of Cl_2O seeded in buffer gases. Photolysis occurs at 308 nm in the stagnation region of the source, prior to expansion through a 100 micron orifice. The chemical composition of the beam is diagnosed by mass spectrometery. Photolysis leads to significant depletion of the parent Cl_2O and formation of ClO which dimerizes rapidly at the high stagnation pressures (200 Torr). By-products include Cl_2, and O_2, as well as residual parent Cl_2O. A number of parameters are critical to ClOOCl formation, including nozzle and photolysis volume dimensions, stagnation pressure and temperature, laser pulse energy, and addition of trace gases to vibrationally relax products. We have found conditions which we believe optimize ClOOCl.

  We have begun photolysis measurements using the beam generated by this source. In our photodissociation experiments to date, we have observed photoproducts from dissociation at 308 nm which cannot be attributed to photolysis of Cl_2O, Cl_2, or ClO, and are consistent with dissociation of ClOOCl. We are currently collecting further data on this system to confirm the identity of the parent molecule and to clarify the nature of the photoproducts, their dissociation dynamics, and their relative yields.

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Laboratory Studies of Reactions and Photochemistry of Halogenated Species That Affect Stratospheric Ozone Abundance

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Research Objectives

This project involves the application of spectroscopy to the study of rates, intermediates, and products of reactions that are important in the Earth's stratosphere. The experiments are carried out using a high resolution Fourier transform spectrometer, a linear photodiode array spectrometer, and a monochromator to obtain IR, visible, and UV spectra of transient and stable species of atmospheric importance. Reaction rate coefficients, absorption cross sections, and reaction mechanisms are investigated. The obtained data helps to improve our knowledge of stratospheric chemistry, to understand the extent and rates of ozone level changes, and to provide spectroscopic data for laboratory and field measurements.

Summary of Progress and Results

- *Gas-Phase Reactions of Halogen Oxides:* Rate coefficients for the IO self-reaction, IO + IO $\rightarrow$ Products (k1) and BrO self-reaction (k2) were determined to be k1= 9.9 $x10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature between 250 and 320 K and k2(T) = 1.6 $x10^{-11}$ $exp(220/T)$ cm^3 $molecule^{-1}$ s^{-1}over the range 203 to 393 K. Absorption spectra for the IO radical between 340 and 480 nm, the absorption cross-section of IO at the peak of the (4,0) band, and the absorption cross-section for BrO at the peak of the (7,0) band were measured as a function of temperature. The rate coefficient for IO + ClO reaction was measured at 5-15 Torr between 200-363 K to be $k(T) = 5.1 \times 10^{-12} \exp(280/T)$ cm^3 $molecule^{-1}$ s^{-1}. Atomic iodine was identified as a major product of this reaction with a yield of 0.8. The information from these three studies quantify the role of halogen oxides, and in particular that of iodine monoxide, in the stratosphere. It also shows the importance of iodine in the troposphere, such as in the marine boundary layer and the Arctic Springtime troposphere.
- *Photochemistry of Halogen Compounds:* The ultraviolet absorption spectra of a number of alkyl iodides found in the troposphere, CH_3I, C_2H_5I, $CH_3CH_2CH_2I$, CH_3CHICH_3, CH_2I_2, and CH_2ClI, were measured over the wavelength range 200 to 380 nm and temperature range 298 to 210 K. The absolute quantum yields of Cl (1.03 ± 0.07 at 193 nm, 0.27 ± 0.02 at 222 nm, and 0.18 ± 0.02 at 248 nm) and Br atoms (1.04 ± 0.13 at 193 nm, 0.86 ± 0.06 at 222

nm, and 0.75 ± 0.13 at 248 nm) in the photodissociation of CF_2ClBr were measured using atomic resonance fluorescence detection of Cl and Br. The CF_2 radical quantum yields in the 193 nm photolysis of CF_2Br_2 and CF_2ClBr were measured to be 1.15 ± 0.30 and 0.91 ± 0.30, respectively. This photochemical data allows calculation of atmospheric photolysis rates, J-values, and the tropospheric lifetimes of these compounds. Therefore, the efficiency of transport of iodine compounds into the stratosphere and the rate and location of the degradation of the Halons in the stratosphere are quantified.

- *Heterogeneous Chemistry of Halogen Compounds:* The interactions of HCl and HOCl on 60 wt% liquid sulfuric acid were studied at 251 to 276 K on bulk sulfuric acid and submicron droplets of sulfuric acid. These results are in very good agreement with theoretical predictions based on measured physico-chemical parameters and extrapolations of other independent results and provide a means for including heterogeneous reactions in numerical models of the atmosphere. Uptake of $BrONO_2$ onto submicron (~0.1 μm radius) sulfuric acid aerosol was studied using a chemical ionization mass spectrometer and found to produce HOBr and HNO_3 very efficiently (γ ~0.8 for H_2SO_4-content < 70 wt%). The equilibrium constant for the gas phase process, $BrONO_2 + H_2O = HOBr + HNO_3$, was measured and the heats of formation of the bromine compounds were deduced. The heterogeneous hydrolysis of $BrONO_2$, followed by photolysis of the HOBr product, is a major source of HO_x in the low stratosphere. This process enhances the deduced ozone depletion ability of bromine in the stratosphere and increases the ODP of all bromine compounds.

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Laboratory Studies of Tropospheric and Stratospheric Reactions

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Research Objectives

The primary objective of this task is to study the rates and mechanisms of key elementary gas-phase reactions important in stratospheric and tropospheric chemistry. A secondary objective is to utilize high resolution spectroscopic methods in the ultraviolet, infrared and microwave regions to obtain structural and spectroscopic information concerning atmospheric molecules.

Summary of Progress and Results

Our work has focused on improving and extending our understanding of gas-phase photochemical and kinetic mechanisms important in stratospheric ozone depletion. The specific areas of research include the following:

- *Photochemistry of Cl_2O, $ClONO_2$ and $BrONO_2$.* We have completed a series of studies of the photodissociation mechanisms of molecules at wavelengths beyond 300 nm. At these wavelengths, many temporary reservoir species absorb very weakly, yet photodissociation in this spectral region is the predominant removal mechanism in the lower stratosphere. We found that for Cl_2O, $ClONO_2$ and $BrONO_2$, broad-band photolysis beyond 300 nm gives rise to pressure-dependent product yields. In the case of Cl_2O, the mechanism involves formation of metastable triplet electronic states which have lifetimes comparable to the collision period. *Ab initio* calculations using a multi-reference method identified several states in the triplet manifold which could be responsible both for the observed pressure dependence, and for transient electronic spectra which appear subsequent to the photolysis pulse. In $ClONO_2$ and $BrONO_2$, the observed pressure dependence in the observed quantum yields could play a role in the partitioning of chlorine and bromine in the lower stratosphere.
- *Kinetics of Gas-Phase Stratospheric Reactions.* We have studied the rates and mechanisms of a number of gas-phase reactions involving radicals in the FO_x, ClO_x and BrO_x families. In the FO_x system we studied reactions of FO and FO_2 radicals with NO, NO_2, O_3 and selected hydrocarbons to determine the efficiency of proposed ozone destruction cycles involving fluorine radicals. The results indicated that these cycles would not significantly perturb the

ozone budget. In the ClO_x system we completed and published our extensive study of the ClO + ClO reaction. This study measured the temperature dependences of the branching ratios for the known bimolecular channels which may be important under certain conditions in the perturbed polar stratosphere. Also, work has commenced on a study of HCl product formation in the OH + ClO reaction. In the BrO_x system we completed a study of the temperature dependence of the HO_2 + BrO reaction. The results suggested that the reaction is about a factor of two slower than previously determined by Poulet *et al.* We have also carried out extensive studies of the rotational, vibrational and electronic spectra of OBrO.

- *Electronic Structure Calculations.* In collaboration with the theoretical chemistry groups of J. Francisco at Purdue University, T. Lee at NASA/Ames Research Center, and I. Williams at University of Bath, we have carried out *ab initio* calculations on several systems of stratospheric interest using Gaussian 92 and other packages running on the JPL Cray YMP-2 and elsewhere. This work has focused on predictions and comparisons of structural parameters with experiments, and calculations of thermochemical parameters. Some of the molecules studied include Cl_2O, FOCl, $HClO_2$, $HClO_3$, $HOClH^+$, $ClO{\bullet}H_2O$ and other species.

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New Atmospheric Ozone and Nitrous Oxide Sources

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Research Objectives

The objectives of the program encompass two general lines of endeavor, linked by emphasis on O_2 photoabsorption. The goals are to better understand the interaction of solar radiation with the atmosphere in the 170-260 nm region. The study therefore involves accurate measurements of absorption linewidths in the O_2 Schumann-Runge bands, determination of absorption strengths in the O_2 Herzberg band systems, investigation of new O_2 absorption band systems in the 240-250 nm region, and a study of a possible stratospheric N_2O source based on O_2 photoabsorption.

Summary of Progress and Results

Over the 1994-1996 period, progress has been made in four areas: linewidth measurements in the O_2 Schumann-Runge bands, absorption measurements on O_2 all the way to the first dissociation limit, new transition probability determinations for the O_2 Herzberg states, and investigations on N_2O formation from the interaction of electronically excited O_2 with N_2.

The first has led to definitive agreement among the three groups conducting such measurements, the second has opened up the study of weakly bound excited states of O_2, the third has led to improved absorption and emission characteristics of the O_2 Herzberg states, and the fourth has provided stringent upper limits on N_2O production from the reaction investigated.

Investigations on the O_2 Schumann-Runge system linewidths were recently conducted in conjunction with studies by Brenton Lewis and colleagues at Australian National University, who used a different experimental technique. Whereas we excited a variety of upper-state levels from vibrationally excited ground-state levels, their approach was to make all measurements from the v = 0 level, using a vacuum UV laser system for excitation, followed by UV fluorescence detection. For studying the lowest levels of the upper state, only our method is successful, but for the higher levels, the two techniques give equivalent results. The group at Harvard-Smithsonian is making synchrotron-based absorption measurements, and we understand that their results are comparable to ours and those of Lewis and colleagues. It appears that their earlier analysis was faulty as a result of assuming an incorrect lineshape for their data. We intend to publish these results jointly.

We collaborated with G. Meijer's group at the University of Nijmegen to use cavity ring-down spectroscopy for measuring weak transitions in O_2 near the dissociation limit, at 242-245 nm. As a result, we added five new Herzberg bands to the literature, including the v = 12 level of the $A^3\Sigma_u^+$ state, which is bound by only ~ 5 cm^{-1}. In addition, we found more than a hundred new absorption lines, which we believe belong to weakly bound states discussed in the literature for many years, but not previously characterized. Although they are weak absorbers, they may have atmospheric significance in the atom recombination process. Meijer's group has started similar measurements on $^{18}O_2$, which will ultimately aid in identifying the new features.

Using cavity ring-down data that we received earlier, we analyzed the Herzberg line- and band-strengths. The analysis provided by Bates several years ago was, we believed, suspect, because it was based on unrealistic calculated transition moments. We reevaluated the absorption strengths and found that substantial changes must be made to the compilation given by Bates [*Planet. Space Sci., 37,* 881, 1989]. A paper in preparation will present improved transition probabilities for the three Herzberg systems as well as the Chamberlain system.

Our earlier studies demonstrating the rapid interaction between O_2 ($A^3\Sigma_u^+$) and N_2 led to an investigation of the magnitude of the quantum yield for stratospheric N_2O production by this mechanism. Although we calculated that a value of only 0.04% would result in a significant contribution to the N_2O burden, results up to the present indicate that an upper limit to the yield is at least an order of magnitude smaller than this figure, for the particular $O_2(A)$ vibrational level studied, v = 9.

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Reaction Rate and Reaction Product Measurements

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Research Objectives

Absolute reaction rate constants for atmospheric reactions are measured and primary reaction products are identified and quantitatively measured, both in as direct a manner as possible. Recent research has emphasized the study of the radical-radical reactions of the halogen oxide radicals XO where X = Cl, Br and I. Supporting photoionization mass spectrometry studies at the National Synchrotron Light Source, Brookhaven National Laboratory, provide spectroscopic and thermodynamic data for the halogen oxide radicals XO and the metastable molecular species HO_X and X_2O.

Summary of Progress and Results

The temperature dependence of the rate constant for the reaction $O(^3P) + HOBr \rightarrow OH+BrO$ (1) has been determined for the first time. Employing the discharge flow technique with collision-free sampling to a mass spectrometer, the results between T = 233 and 423 K demonstrate that the reaction has a small energy barrier and that the rate constant is well represented by the expression $k_1 = (1.4\pm0.5) \times 10^{-10} \exp(-430\pm260/T)$ cm^3 molecule^{-1}s^{-1}. This gives an HOBr loss rate due to reaction with atomic oxygen of about 5×10^{-4}s^{-1} at 25 km which is comparable to the photolysis rate J(HOBr). Implications for HOBr loss in the stratosphere have been tested using a 1-D photochemical box model in collaboration with Ralf Toumi (now at Imperial College, London University). With the inclusion of our rate parameters and products for O+HOBr, calculated concentration profiles of the BrO radical increased by up to 33% at an altitude of 35 km. It is clear that the reaction between atomic oxygen and HOBr needs to be included in global atmospheric chemistry models.

The reaction $OH+BrO \rightarrow Br+HO(2)$ is potentially important in the partitioning of stratospheric bromine. There have been no reported experimental measurements of k_2 although an estimate of $k_2 = 1 \times 10^{-11}$ cm^3 molecule^{-1}s^{-1} at T = 298 K is given in the 1994 NASA kinetic data evaluation. In collaboration with Denis Bogan (now at NASA Headquarters), we have made the first

measurement of the rate constant for OH+BrO and employed a recently built "nested injector" flow reactor. These were difficult experiments and it was impossible to isolate reaction (2) from the competing reactions OH+Br_2 and BrO+BrO. From profiles of [BrO] as a function of time and numerical integration of coupled kinetic rate equations, we obtain $k_2 = (7.5\pm3.0)\times10^{-11}$ cm^3 $molecule^{-1}s^{-1}$ at T = 300 K by parameter fitting k_2 to the kinetic model. This experimental result is about one-half the collision rate and is seven times larger than the estimated value. Our result is consistent with trends observed in the reactions of HO_2 with ClO and BrO.

Thermochemical calculations show that only two product channels are possible: (2a) Br+HO_2 and (2b) HBr+O_2, which is a 4-centered elimination reaction. Both of these product channels are expected to proceed through a vibrationally excited adduct HOOBr*. The partitioning between the two product channels will be determined by the competition between the breaking of a simple O-Br bond in the HOOBr adduct, channel (2a), and the 4 centered elimation of HBr, channel (2b). By estimating the enthalpy of formation of the HOOBr adduct and the activation energies and Arrhenius A factors for each channel, Br+HO_2 is expected to be the major product channel. However, a small contribution from the channel yielding HBr+O_2 cannot be discounted.

On the basis of observed trends in the rate constants for reaction of HO_2 with ClO, BrO and IO and our new result for OH+BrO, we estimate that k(OH+IO) = 1 to 2×10^{-10} cm^3 $molecule^{-1}s^{-1}$ at T = 300 K, a value comparable to the collision rate. There are no experimental measurements of this rate constant. In the reaction of atomic oxygen with C_2H_5I, we observed the photoionization signals due the products HOI and IO to be in the ratio 7.6 to 1.0 at a wavelength of 120 nm (10.3 eV). While C_2H_5I may be of little importance in upper atmospheric chemistry, there results confirm that its reaction with O is an unexpected laboratory source of HOI.

Using a discharge flow-photoionization mass spectrometer apparatus with dispersed synchrotron radiation as the ionizing source, we have collaborated with Bruce Klemm and his associates at the National Synchrotron Light Source, Brookhaven National Laboratory, on measurements of the photoionization spectra, ionization energy and heat of formation of several free radical and metastable molecular species of atmospheric interest. During the last 3 years we measured the following ionization energies: IE(FO) = 12.78 eV, IE(ClO) = 10.88 eV, IE(IO) = 9.73 eV, IE(Cl_2O) = 10.91 eV, IE(Br_2O) = 10.26 eV, IE(HOCl) = 11.12 eV and IE(HOI) = 9.81 eV. This information is very useful for unambiguously identifying reaction products in laboratory experiments, especially for species such as the above which are impossible, or at best difficult, to detect by sensitive optical techniques such as laser induced fluorescence. We also obtained the following values for the T = 298K heat of formation for the indicated species: ΔHf (FO) = 26.2 kcal mol^{-1}, ΔHf (IO) = 30 kcal mol^{-1}, ΔHf (Cl_2O) = 18.5 kcal mol^{-1}, ΔHf (Br_2O) = 25.6 kcal mol^{-1}, ΔHf (HOCl) = -18.3 kcal mol^{-1}, ΔHf (HOBr) = -14.3 kcal mol^{-1}, and ΔHf (HOI) = -11 kcal mol^{-1}. Such data are important in evaluating the exothermicity (or endothermicity) of potentially significant atmospheric reactions.

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Laboratory Studies of Homogeneous and Heterogeneous Stratospheric Reactions Involving Halogenated Reservoir Species

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Research Objectives

This project involved the measurement of kinetics and quantum yields relevant to the stratospheric chemistry of the halogenated reservoir species $ClONO_2$, $BrONO_2$, HCl and HOBr. Some rate coefficients for reactions of chlorine atoms with atmospherically important species were measured using both time-resolved and relative rate techniques.

Summary of Progress and Results

- Chlorine Nitrate Quantum Yields: Resonance fluorescence has been used to determine quantum yields for Cl (~0.7), ClO (~0.3) and O (<0.05) in the photolysis of chlorine nitrate at 308 nm. Use of a strongly reversed lamp showed that roughly 1/3 of the Cl atoms were formed in the excited $Cl(^2P_{1/2})$ state. The addition of NO enabled ClO to be detected as Cl.
- HOBr and Br_2O Absorption Cross Sections: The ultraviolet absorption cross sections of Br_2O and HOBr have been measured for the first time using a diode array spectrometer. Br_2O was produced from the reaction of Br_2 with HgO, and, after equilibration with water vapor, features due to HOBr could also be identified. From the mass balance in the system, a value for the equilibrium constant for $2HOBr \leftrightarrow Br_2O + H_2O$ could be derived, enabling estimates of the heats of formation of HOBr and Br_2O to be made.
- Quenching of $Cl(^2P_{1/2})$ Atoms: Spin-orbit excited chlorine atoms were produced in the photolysis of either NOCl or $ClONO_2$, and their rates of relaxation by various gases were measured. The rate coefficient for quenching by helium is unusually large, $6x10^{-14}$ cm^3 $molecule^{-1}s^{-1}$. The removal of $Cl(^2P_{1/2})$ by CH_4 was shown to be due to physical quenching, and not to enhanced reactivity as compared to the ground state.
- Rate Coefficients for the Reaction of Cl Atoms with Acetonitrile: The rate coefficient for the reaction of chlorine atoms with acetonitrile has been measured between 273 and 333 K using both flash photolysis with resonance fluorescence detection and the relative rate technique. The rate coefficient for this reaction was previously thought to be negligible at room temperature

and below. The reaction was shown to proceed predominantly by hydrogen atom abstraction. Rate coefficients were also obtained for the reaction of F atoms with CH_3CN. The rate coefficient was found to be pressure dependent.

- Rate of Decomposition of Bromine Nitrate: The thermal decomposition of bromine nitrate has been measured as a function of temperature (range 320-340 K) at 700 Torr, and as a function of pressure at 330 K. The results were combined with rate coefficients for the reverse reaction to give equilibrium constants, and thus a value for the heat of dissociation of $BrONO_2$. The $BrO-NO_2$ bond is found to be a little stronger than the analogous bond in chlorine nitrate. A consistent set of thermochemical data for bromine-containing compounds is proposed. A rate coefficient of $5x10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} was measured for the reaction of Br atoms with bromine nitrate.
- Reaction of OH with ClO: A flash photolysis experiment with tunable diode laser detection has been set up to measure the yield of HCl in the reaction of OH with ClO. Concurrent experiments using resonance fluorescence will be used to verify that the source chemistry for producing OH and ClO is understood. The system has been used to measure the rate coefficients for the reactions of Cl atoms with C_2H_6 and CH_3CHO by monitoring HCl in real time. The production of vibrationally excited HCl with a yield of approximately 50% has been demonstrated in the latter case.

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Laboratory Studies of Heterogeneous Processes in the Stratosphere

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Research Objectives

Heterogeneous reactions on the surfaces of polar stratospheric cloud particles are now recognized to play a major role in the annual appearance of the Antarctic ozone hole. In an analogous manner, heterogeneous reactions on the sulfate aerosol particles found throughout the global stratosphere may affect global stratospheric chemistry. The objective of this research program is to measure uptake rates and solubilities of trace atmospheric species on sulfuric acid surfaces at temperatures and compositions representative of the stratosphere.

Summary of Progress and Results

The heterogeneous reactions (1) through (5) on polar stratospheric cloud particles are now thought to be key contributors to the photochemical mechanism responsible for the Antarctic ozone hole:

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \quad (1)$$

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \quad (2)$$

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \quad (3)$$

$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3 \quad (4)$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O \quad (5)$$

We use a low pressure Knudsen cell flow reactor to measure reaction rates and solubilities of trace species on sulfuric acid solutions at stratospheric temperatures and compositions in order to determine the impact of these reactions on the global stratosphere.

The solubility of HCl will determine how much of the second reactant in reactions (3) to (5) is available in the sulfate aerosol particles. We have measured the solubility of HCl in 50 to 60 weight percent sulfuric acid solutions between 220 and 230 K. We have found that, given the small amount of gas phase HCl in the stratosphere, the amount of HCl dissolved in the aerosol particles is small and reactions (3) to (5) are unlikely to be important for local heterogeneous processing of chlorine at mid-latitudes.

Bromine heterogeneous chemistry analogous to Reactions (1) to (5) may also be important in the stratosphere. We have measured the solubility of HBr in 60 to 72 weight percent sulfuric acid solutions between 205 and 240 K. The solubility of HBr is approximately two orders of

magnitude higher than the solubility of HCl at a given temperature and sulfuric acid concentration. However, HBr is several hundred times less abundant than HCl in the stratosphere, so that the amount of HBr dissolved in aerosol particles will be quite small.

It is possible that other reactions besides (1) to (5) occur rapidly on sulfuric acid surfaces and affect the chemical balance of the stratoshere. In particular, little is known about how heterogeneous reactions might affect the odd-hydrogen family. Formaldehyde is one molecule closely connected to odd-hydrogen. If heterogeneous removal of formaldehyde were fast enough to compete with gas-phase destruction, the net result would be a decrease in odd-hydrogen. We have measured the uptake of formaldehyde on 60 to 75 weight percent sulfuric acid solutions over a temperature range of 205 to 235 K and found it to be large and irreversible.

Publications

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Laboratory Investigations of Stratospheric Halogen Chemistry

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Research Objectives

The primary objective of this project has been application of state-of-the-art experimental methods to investigate the kinetics, mechanisms, and thermochemistry of gas phase chemical reactions which play important roles in the atmospheric cycles of chlorine, bromine, and iodine. Secondary objectives include contributing to our overall understanding of atmospheric chemistry and chemical reactivity.

Summary of Progress and Results

One focal point of our research effort has been the application of chemical kinetics studies to evaluation of free radical thermochemistry. Recently, we have discovered that reactions of chlorine atoms with haloalkanes have addition pathways which, under atmospheric conditions of temperature and pressure, can be much faster than competing hydrogen transfer, halogen transfer, and/or halogen substitution pathways. Through direct observation of association - dissociation kinetics and associated second- and third- law analyses of the equilibrium data, bond strengths have been evaluated for $Cl(^2P_j)$ adducts with CH_3I, CH_3Br, CF_3I, CD_3CD_2I, and CF_3CH_2I. *Ab initio* calculations by our collaborator M. L. McKee of Auburn University reproduce experimental bond strengths quite well and predict structures where the C - X - Cl bond angles are close to 90° (X = I or Br). An excellent inverse correlation exists between observed (or calculated) adduct bond strengths and the haloalkane ionization potential. Both the dependence of observed bond strengths on haloalkane ionization potential and the theoretical bond angles are consistent with the formation of 2 center - 3 electron bonds involving interaction between the singly occupied orbital of the chlorine atom and the highest (doubly) occupied molecular orbital of the haloalkane. Further research is needed to examine the potential importance in atmospheric chemistry of radical - haloalkane adducts.

A second focal point of our research effort has been photochemistry studies of interest for understanding stratospheric chemistry. Carbonyl sulfide (OCS) is thought to be an important photolytic precursor for the background, i.e., non-volcanic, lower stratospheric sulfate aerosol layer. We employed time-resolved detection of CO by tunable diode laser absorption spectroscopy to measure the quantum yield for CO production from 248 nm photodissociation of OCS. We found that the quantum yield is greater than 0.95 and most likely unity. This result suggests that the contribution of OCS as a precursor to the lower stratospheric sulfate aerosol layer is somewhat larger than previously thought. Currently, we are investigating the photochemistry of bromine nitrate ($BrONO_2$); the role of this key reservoir species in stratospheric chemistry depends critically on the identity of the photodissociation products. We find that the 266 nm quantum yields for Br and BrO production are similar in magnitude and sum to a value which is unity within experimental uncertainty. The Br + $BrONO_2$ reaction is fast, i.e., about one-third of the gas kinetic collision rate. Our studies of $BrONO_2$ photochemistry are being extended to a longer photolysis wavelength, i.e., 355 nm.

The third focal point of our research effort has involved development of flash photolysis schemes for studying radical - radical reaction kinetics and implementation of these schemes for studying radical - radical reactions of stratospheric interest. We carried out the first direct study of O + BrO kinetics using a novel dual laser flash photolysis technique with time - resolved, simultaneous detection of both reactants. We found that under typical mid-stratospheric conditions, the O + BrO rate coefficient is considerably faster than suggested by earlier "guesstimates." The O + BrO catalytic cycle appears to be the most important BrO_x cycle for odd-oxygen destruction at altitudes above 24 km. Our most recent efforts in the area of radical-radical reaction kinetics have focused on the HO_2 + BrO reaction. Development of a clean flash photolysis scheme for studying HO_2 + BrO kinetics has proven to be challenging. Multiple kinetic schemes have been tried. While results obtained to date are not completely satisfactory, our data do support a relatively slow 298K rate coefficient in the range (1 - 1.5) x 10^{-11} $cm^3molecule^{-1}s^{-1}$. Our studies of HO_2 + BrO kinetics are continuing; the most promising kinetic scheme currently under investigation involves 351 nm laser flash photolysis off $Cl_2/CH_3OH/O_2/Br_2/NO_2$ mixtures.

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Laboratory Studies of Chemical and Photochemical Processes Relevant to Stratospheric Ozone

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Research Objectives

The purpose of this project is to reduce the uncertainty in several key gas-phase and heterogeneous-phase kinetic processes which impact our understanding of stratospheric ozone. The main emphasis of this work is on measuring rate coefficients and product channels for reactions of HO_x and NO_x species in the temperature range 200 K to 240 K relevant to the lower stratosphere. Other areas of study have included infrared spectroscopic studies of the HO_2 radical, measurements of OH radical reactions with alternative fluorocarbons, and determination of the vapor pressures of nitric acid hydrates under stratospheric conditions. The results of these studies will improve models of stratospheric ozone chemistry and predictions of perturbations due to human influences.

Summary of Progress and Results

HO_2 Radical Reaction Kinetics

The reaction of HO_2 with ozone is one of the important ozone controlling reactions in the lower stratosphere. We have studied the reaction rate and mechanism rate at temperatures characteristic of the lower stratosphere using infrared absorption spectroscopy of isotopically labeled HO_2 radicals. The study investigated the fraction of OH produced via hydrogen abstraction versus that produced via oxygen abstraction as a function of temperature. The conclusion of the work is that H atom abstraction is the dominant pathway from room temperature down to stratospheric temperatures and that variation in this aspect of the reaction mechanism does not account for the previously observed curvature in the $HO_2 + O_3$ Arrhenius plot.

HO_2 Quantitative Spectroscopy Studies

Infrared spectroscopy provides a specific and sensitive method for detecting the HO_2 radical in laboratory studies and is a potential method for direct measurements in the stratosphere. We have augmented our previous work on line position and line strengths by measuring the pressure broadening coefficient in air for infrared transitions of HO_2 in the v_2 vibrational band around 1400 cm^{-1}. The measured an air broadening coefficient (0.107 $\pm$0.009 cm^{-1} atm^{-1} for the $9_{19} \leftarrow 8_{18}$

F_1,F_2 doublet (1411.180 cm^{-1}) in the v_2 band) has direct implications for the design and interpretation of atmospheric monitoring experiments for the hydroperoxyl radical.

OH Reaction Rates with Alternative Halocarbons

Hydrogen-containing halocarbons are being used as alternatives for fully halogenated compounds since their higher reactivity with OH radicals in the lower atmosphere limits their transport to the stratosphere and their resultant degradation of the ozone layer. Room temperature reaction rates with OH were measured for six fluoropropanes, one fluorobutane and one fluoropentane. High purity samples of these species were provided by Allied Signal Corporation who also partially sponsored this work. The room temperature reaction rates vary by a factor of ~100 for the different species and show the dramatic deactivation associated with F substitution. The temperature dependence for the reaction of OH with $CF_3CH_2CF_2CH_2CF_3$ was measured at temperatures between 278 and 354 K. The data is fit well by an Arrhenius expression with A = (1.28 ±0.7) x 10^{-12} cm^3 $molecule^{-1}s^{-1}$ and E/R = 1833 ±250 K.

Thermodynamic Studies of Nitric Acid Hydrates at Stratospheric Temperatures

The importance of heterogeneous chemical reactions on stratospheric aerosol surfaces has been vividly demonstrated by measurements and models of the polar stratosphere. We have determined the thermodynamic parameters for nitric acid mono-, di-, and tri- hydrates by vapor pressure measurements of water and nitric acid in equilibrium with the solid phases using tunable diode laser spectroscopy. Our experiments indicate that nucleation and persistence of the metastable $HNO_3 \bullet 2H_2O$ may be favored in polar stratospheric cloud over $HNO_3 \bullet 3H_2O$ even though the later is thermodynamically more stable under typical stratospheric conditions of temperature, water vapor and nitric acid vapor.

We have continued these studies of nitric acid hydrates relevant to polar stratospheric cloud formation by investigating mixtures with sulfuric acid. Formation of crystalline phases of H_2SO_4, HNO_3 and H_2O were studied at stratospheric temperatures and vapor pressures. Freezing of supercooled solutions began at < 200 K by crystallization of x $\bullet H_2SO_4 \bullet HNO_3 \bullet H_2O$, where x is presently undetermined, followed by a progression of metastable phases. Metastable $HNO_3 \bullet 3H_2O$ formed in some experiments. Large particles are readily produced from metastable phases, providing a mechanism for removal of HNO_3. Mixed crystals partially melted at 200 K, forming [$H_2SO_4 \bullet 4H_2O$ + ternary solution], a potentially important process in the arctic polar vortex.

Ab Initio and Thermodynamic Studies of the Water-Nitric Acid Complex

Nitric acid is an important trace gas both in the stratosphere and the troposphere. If a significant fraction of the atmospheric nitric acid were complexed with water, it might affect several important problems in the upper troposphere and lower stratosphere. The nitric acid-water complex has been studied by high level ab initio calculations. The equilibrium structure of the complex has an asymmetric doubly hydrogen-bonded ring. A strong hydrogen bond is donated by the hydroxyl group of nitric acid to the oxygen atom of water, and a much weaker hydrogen bond is donated by an OH bond of water to a second oxygen of nitric acid. The HNO_3 unit in the complex is considerably distorted with the OH stretching frequency red-shifted by over 300 cm^{-1} from the isolated molecule and the infrared intensity enhanced by an order of magnitude. The binding energy of the complex is calculated as De = -9.5 kcal/mol. The equilibrium fraction of nitric acid

complexed with water is predicted to be near 1% at the Earth's surface and decreases with the increase of altitude.

NASA Data Evaluation Panel

C. E. Kolb has served on NASA's Panel for Data Evaluation as the panel's lead member responsible for heterogeneous processes. The heterogeneous chemistry section of the biennial review, Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, first introduced in 1990, has been completely revised and significantly expanded in the eleventh [DeMore *et al.*, 1994] edition. The Heterogeneous Chemistry section now includes three data tables covering Mass Accommodation Coefficients, Gas/Surface Reaction Probabilities, and Henry's Law Constants for Gas-Liquid Solubilities, as well as text and extensive notes presenting background and guidance for using the tables. The eleventh edition of the Heterogeneous Chemistry section presents and evaluates the work for over eighty new or revised archival publications beyond the tenth edition.

Publications

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B. SPECTROSCOPY

Quantitative Infrared Spectroscopy of Minor Constituents of the Earth's Atmosphere

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Research Objectives

We obtain quantitative laboratory spectroscopic measurements of molecular constituents which are of importance in understanding the "health" of the Earth's atmosphere, and in particular emphasize those species which are important for understanding stratospheric kinetics or are used for long term monitoring of the stratosphere. Our measurements provide: (1) line and band intensity values which are needed (a) to establish limits of detectability for as yet unobserved species, and (b) to quantify the abundance of those species which are observed; (2) line-positions,-half widths and pressure induced shifts are all needed for remote and *in situ* sensing techniques; and (3) data on the above basic molecular parameters at temperatures and pressures appropriate to the real atmosphere.

Summary of Progress and Results

During the previous year, O_2 pressure broadened spectra of the NO vibration-rotation fundamental were obtained using a flow system. These spectra will be analyzed for O_2 broadening coefficients. High quality 0.005 cm^{-1} resolution spectra of HNO_3 were obtained in the 1100 cm^{-1} - 2700 cm^{-1} spectral region. Rovibrational line intensities on these spectra will be determined to support the OPTIMA experiment. An experimental feasibility study was completed for using magnetic rotation spectroscopy (MRS) to detect free radical molecular species (*in situ*) in the part per trillion mixing ratio range. We have concluded that MRS holds promise for a next generation of free radical detectors. Analysis for the electric dipole moment function of the ground electronic state of the OH molecule was completed using a very large set of relative emission lines of the Meinel system. A definitive and comprehensive compilation of rovibrational intensities for the CO molecule in its various isotopic forms was published.

Publications

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Tunable Far-Infrared Studies in Support of Stratospheric

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Research Objectives

This is a research program of spectroscopic studies for the support and analysis of atmospheric measurements. It includes fully line-resolved measurements of submillimeter and far infrared spectroscopic line parameters (pressure broadening coefficients and their temperature dependences, and line positions) for the analysis of field measurements of stratospheric constituents, far infrared database improvements, and studies for improved satellite measurements of the earth's atmosphere. This research program is designed to enable the full utilization of spectra obtained in far infrared/submillimeter field measurements, such as FIRS-2, FILOS, IBEX, SLS, EosMLS, and proposed NASA and European Space Agency measurements of ClO and OH, for the retrieval of accurate stratospheric altitude profiles of key trace gases involved in ozone layer photochemistry.

Summary of Progress and Results

We have extended the development in ultra-high resolution far infrared spectroscopy using the TuFIR laser-mixing method to include:

- Development of radical source chemistries, allowing us to measure pressure broadening and line positions of free radicals (e.g., OH, HO_2, and ClO);
- Development of a novel laser difference technique employing the mixing of CO_2 and NH_3 laser lines, potentially capable of provide tunable radiation covering the 200 to 400 cm^{-1} region (currently being refined). This region of the atmospheric spectrum that has not yet been fully exploited, partly due to limitations in the spectroscopic database which we are now addressing;
- Development of software to perform multiple linear regressions to obtain line broadening and/or shifting information from studies employing complex source chemistries;

- Development of Hamiltonian fitting capability that includes asymmetric top molecules with electron spin-rotation interactions, up to high degree in centrifugal distortion, and including nuclear hyperfine (spin-spin dipolar, Fermi contact, and nuclear quadrupole) interactions.

We have performed spectroscopic studies and data analyses, and updated line databases for numerous molecules, including HO_2, OH, H_2O, H_2O_2, O_2, O_3, and ClO. This includes a re-fitting of the HO_2 spectrum (in collaboration with scientists from Canada and Germany) for states up to N = 30 and Ka = 9, by including combination differences from the lowest electronic transition along with the microwave, millimeter wave and far infrared measurements. A major update of the line parameter listings for OH, HO_2, and H_2O_2 has just been completed, for inclusion in the SAO far infrared line parameter listing.

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Millimeter and Submillimeter Spectroscopy in Support of Upper Atmospheric Research

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Research Objectives

A program of millimeter and submillimeter spectroscopy research is conducted in support of upper atmospheric research. This includes laboratory studies, critical analysis of data from all available sources, generation of line list catalogs, and distribution of results to the field measurement community. The program involves the acquisition and analysis of molecular spectral parameters which are required for the interpretation of data from stratospheric measurements. The laboratory spectral measurements specifically support the JPL millimeter radiometer instruments. In order to take full advantage of spectroscopic techniques for quantitative atmospheric measurements, emphasis is placed on performing accurate line frequency, line width, and transition moment measurements. A large portion of the spectral data is also of value to other groups which use spectroscopic techniques for atmospheric measurements. These data are cataloged in a continuously upgraded millimeter database and made available to interested users. This program also provides rotational spectra of ground and excited states of molecules whose infrared spectra are observed in the upper atmosphere. The fitting algorithms developed for this program are also used to analyze vibrational spectra. In addition, this program provides valuable molecular structural and reaction product distribution information which has direct bearing on proposed mechanisms for polar ozone destruction. Elucidation of the molecular properties of the halogen oxides and oxo-acids is a continuing objective of these investigations.

Summary of Progress and Results

A new edition of the JPL *Microwave Millimeter and Submillimeter Spectral Line Catalog* has been published. The new version of the catalog contains the frequencies, estimated uncertainties, intensities, lower state energies, and assignments for 1,448,153 spectral lines of 298 atomic or molecular species. The database for a number of atmospheric species has been improved.

During the 1994-1996 time period the following laboratory studies have been carried out. The analysis of the ν_1 band of HOBr has been published and the ground state parameters refined.

Further analyses of DOBr infrared and millimeter spectra have allowed a slight refinement of the equilibrium structure and the determination of the harmonic force field for HOBr. The HOBr rotational spectrum has been accurately calculated for the JPL database. Work has been completed on the rotational spectra of the three main isotopic species of Br_2O. The rotational spectrum of OBrO has been observed and analyzed. A preliminary account of the work on the Br_2O and OBrO has been accepted for publication. The Br_2O and OBrO studies represent the first high resolution gas phase spectral studies of bromine oxides other than BrO. The structures and molecular parameters have been determined.

Observations of the rotational spectrum of BrO have been extended and improved. The rotational spectrum of the $^2\Pi_{1/2}$ state has been observed for the first time. Details of the molecular bonding and the shape of the interatomic potential have been elucidated. Additional measurements have been made on the rotational spectrum of $ClONO_2$. The molecular constants have been significantly improved providing a more accurate database for predicting its atmospheric spectrum. The work on the rotational spectrum and structure of chlorine chlorate, Cl_2O_3, has been completed and published. Work on the excited vibrational state of O_2 in its $a^1\Delta_g$ electronic state as well as its ^{18}O substituted species has been completed and published. This study has led to an improved calculation of the $^{16}O^{18}O$ spectrum for the JPL catalog. The calculated spectra for the mono-substituted ^{17}O ozones have been improved and added to the Catalog. This work along with a related analysis for ^{17}OSO has been published. The O_2 and N_2 pressure broadening coefficients of the several HNO_3 transitions near 204 GHz have been measured in the 200--300K temperature range. These transitions are being used by the UARS-MLS for monitoring global HNO_3. This work was done in collaboration with the group at Ohio State University which independently measured many of the same transitions to assure accuracy. Additional measurements of the rotational spectrum of ClO in its ground and first excited vibrational state were made in the 632 to 725 GHz region. These measurements have been published in a paper which also describes our measurements of the O_2 and N_2 broadened linewidths of ClO. Additional analyses of the rotational spectrum of $HClO_4$ are continuing. This work has been presented at symposia and is being prepared for publication.

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Millimeter and Submillimeter Spectroscopy of Molecules of Atmospheric Importance

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Research Objectives

It has been demonstrated that remote-sensing techniques based upon millimeter, submillimeter and infrared technology can make important contributions to atmospheric science. The planning, execution, and interpretation of those experiments require a firm knowledge of the spectroscopic properties of atmospheric molecules. Our work is designed to support these atmospheric observations via contributions to the spectroscopic database for the microwave through infrared spectral region. The work includes both the direct measurement of spectra of important atmospheric species and the calculation of synthetic spectra from these measurements. Results include line positions, linewidths, and intensities in both the ground and excited vibrational states.

Summary of Progress and Results

We have carried out measurements of line positions, widths, and intensities in the millimeter, submillimeter, and infrared spectral regions and have done theoretical calculations in support of these measurements. In addition, we have just completed the development of a new type of spectroscopic system which significantly increases the capability of mm/submm measurements to impact the rotation-vibration database which supports remote sensing observations. Molecular species studied include N_2O_5, HNO_3, $ClONO_2$, H_2S, HDO, H_2O, HOOH, and SO_2.

Our mm/submm spectroscopic work on the rotational structure of excited vibrational states is designed to contribute to both the pure rotational and rotational-vibrational databases. In HNO_3 our work has included studies of the ν_3/ν_4, $\nu_5/2\nu_9$, $3\nu_9$, and ν_9 states. The work on the states which interact with the torsional motion has been especially interesting because we have discovered that the perturbations which couple these states to other states also couple the torsional splittings into their spectra. This work has been carried out in close cooperation with infrared workers so that the resultant analyses are fully representative of both the pure rotation and vibration-rotation spectra. In HOOH we have completed studies in the n = 0 and n = 1 torsional states of the ground vibrational state and the pure rotational spectrum of the ν_3, n = 0 state. Because the interactions

between internal rotation and vibrational states lead to a complex interacting spectrum, these, too, have been the objects of considerable infrared study. One of the important features of our analyses is that they simultaneously account for both the infrared and mm/submm data to their respective experimental accuracies. In addition, the mm/submm spectrum of $ClONO_2$, its Cl quadrupole tensor, and its harmonic force field have been studied in collaboration with the JPL group. More details of this work are given in Goyette *et al.* [1994, 1996]; Petkie *et al.* [1994]; Paulse *et al.* [1996]; Muller *et al.*; Paulse [1995]; Pearson [1995]; and Petkie [1996].

N_2O_5, along with its main decomposition products N_2O_4 and HNO_3, has been observed in the infrared [in collaboration with B. P. Winnewisser and M. Winnewisser in Giessen, Germany]. A careful analysis of these decomposition products is necessary in order to obtain accurate, temperature dependent absorbance cross sections because the spectra of the nitrogen oxides is both complex and unstable. This work resulted in reliable values for the absolute absorbance cross sections for the band systems centered at 350 cm^{-1} and 570 cm^{-1}. The results of this work are described in more detail in Siebert *et al.* [1996].

We have also carried out pressure broadening in HNO_3, HDO, H_2S, and SO_2 in the 100 to 600 K region. We have studied collisions both with the atmospherically significant N_2 and O_2 as well as with He and H_2, the latter providing a wider information base for the benchmarking of theoretical methods. These measurements are particularly noteworthy because their temperature range provides an unusually good test for theory. Additionally, the SO_2 and HNO_3 studies provide direct measurements for the recovery of profiles from atmospheric observations. More details of this and related work are given in publications Goyette *et al.* [1993]; Everitt and De Lucia [1995]; and Ball *et al.* [1996].

Finally, we have just completed the development of a new type of BWO based mm/submm spectrometer which has the sensitivity and subdoppler resolution of phase locked spectrometers, but which has the additional capability of recording large spectral regions in only a few seconds. As an example, it was possible to record in the 250 to 350 GHz region ~400 lines of the ν_7 state of HNO_3 in 12 seconds, with automatic frequency measurement and spectral assignment. Previously about 50 lines of this state had been measured in this region. Additionally, the system provides fast pressure broadening measurement capabilities. This system and results based on it are described in Petkie [1996].

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Accurate Absorption Cross Section Measurements for Alternate Halocarbons

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Research Objectives

The emphasis of our task is an accurate determination of the temperature dependencies of the ultraviolet absorption cross sections of halocarbons important in the photochemistry of the upper atmosphere. The temperature dependent cross section measurements have been performed over a wide spectral range (160 nm to 360 nm) and temperature range (~220 K to 350 K) and lend increased confidence in the atmospheric lifetime calculations for the important industrial halocarbon molecules. To accurately measure very small cross sections, we have developed and adopted several alternative approaches, such as the determination of the absorption cross sections the liquid phase and the conversion of the liquid phase values to effective gas phase cross sections. The utility of this technique has been demonstrated in several papers from our laboratory and pioneered the use of the liquid phase for accurate determination of the very low absorption cross sections of halocarbons. In addition, when possible, we extend the temperature dependent cross section determinations to short wavelengths where most hydrocarbon molecules have highly structured spectra with sharp and intense absorptions. The evaluation of the effect of temperature on the ultraviolet absorption spectra often yields valuable information concerning the dynamics of photo-absorption and the electronic and vibrational transitions contributing to the spectra.

Summary of Progress and Results

Absorption cross sections for most volatile compounds which potentially contribute to ozone depletion and global warming, are very low in the solar spectral region and have historically been very difficult to measure accurately. During the course of this program we have carried out a detailed and systematic study of the factors impacting gas phase cross section measurements. These included contribution of scattered light, window adsorption, drift in the intensity of monitoring light, etc. The quantification of the effects of instrumental scattered light has been very important, and will have a major impact in more accurate evaluation of photolysis rates for species with absorptions that extend beyond about 250 nm.

During the course of fiscal years 1994 to 1996, we have determined accurately temperature dependencies of the absorption cross sections for numerous halocarbons including those for CF_3I, CH_3I, CH_3CCl_3, CF_3CHCl_2 (HCFC-123), CH_3CF_2Cl (HCFC-142b), CF_2ClCF_2CHFCl (HCFC-225cb), CF_3CH_3 (HFC-143a) and CH_2ClBr.

In addition, in support of the research activities of scientists, here at NIST, working on the determination of the chemical reactivity of a series of fluorinated halocarbons of importance to upper atmosphere, we have measured the ultraviolet absorption cross sections of CF_3-CH_2-CHF_2, CF_3-CF_2-CH_3, CF_3-CH_2-CF_3, CH_2= CF-CF_3, CH_2= CH-CF_3 and several fluorinated ethers. The accurate cross section data were used to identify and quantify very low level of impurities (in the order of part-per-million) in some of the samples used for reaction rate determinations with the OH radical. In general, the absorption cross sections for the above saturated fluorinated molecules, in the wavelength range 160 to 240 nm, are very low (less than 1.0E-21 cm^2 $molecule^{-1}$). However, the fluorinated olefinic hydrocarbons absorb very strongly the UV radiation on the same wavelength range (with cross sections in the order of 4.0E-17 cm^2 $molecule^{-1}$). Thus by employing the ultraviolet absorption spectroscopy a very low level of olefinic impurities can be detected in the samples of saturated molecules. Even very low level of these impurities in samples of saturated halocarbons can significantly hinder accurate determination of the reaction rate constants. Following the purification of the contaminated samples and removal of the olefinic hydrocarbons our colleagues have determined more accurate rate constants for reactions of saturated fluorinated hydrocarbons with OH radical.

Publications

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High-Resolution Infrared Spectroscopic Studies of Atmospheric Molecules

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Research Objectives

The high-resolution infrared and microwave spectra of known and potential atmospheric molecules are investigated to determine line positions and intensities, collision-induced absorption strengths, and spectroscopic constants for atmospheric monitoring applications, for modeling atmospheric absorption profiles and thermodynamic properties, and for providing experimental benchmarks for theoretical calculations of these properties.

Particular emphasis has been placed on the measurement of the rotationally resolved spectra of molecules containing NO_2 groups ($ClONO_2$, N_2O_5, N_2O_4, and N_2O_3), the collision-induced absorption spectra of N_2 and O_2 and the continuum absorption spectrum of H_2O, the infrared spectra and band intensities of hydrofluorocarbons (HFCs), and the vibrational spectra and intensities of various bands of SO_2, OClO, and HOCl.

Summary of Progress and Results

Infrared spectra of the ν_{12} band of $ClONO_2$ at 1292 cm^{-1}, the ν_{13} band of N_2O_3 at 1304 cm^{-1}, the ν_9 and ν_{11} bands of N_2O_4 at 1757 and 1261 cm^{-1}, respectively, and the ν_{12} band of N_2O_5 at 1246 cm^{-1} were measured at rotational temperatures between 20 to 30 K using a slit-nozzle molecular-beam diode-laser spectrometer. The high resolution and spectral simplicity of the molecular-beam spectra allow complete unambiguous spectral assignments to be obtained for $ClONO_2$, N_2O_3, and N_2O_4. For $ClONO_2$ the resulting spectroscopic constants have been combined with estimates for hot-band constants to simulate the temperature dependence of the 1292 cm^{-1} band shape over a range of conditions appropriate for the stratosphere.

The microwave spectrum of the weakly dipolar N_2O_5 molecule has been obtained at 2 kHz resolution using a Fourier-transform microwave spectrometer. The microwave spectrum demonstrated that the molecule has C_{2h} symmetry and a low frequency (several GHz) tunneling motion associated with the geared rotation of the two equivalent NO_2 groups about their twofold axes. The barrier to this motion is on the order of 10 cm^{-1}. The high-resolution results show that the previously reported microwave spectrum of N_2O_5 observed in a thermal equilibrium waveguide cell is most likely a contaimament molecule. Partially resolved molecular-beam infrared spectra of the 1246 cm^{-1} band reveal a dense spectrum characteristic of molecules undergoing intramolecular vibrational energy redistribution (IVR).

Collision-induced absorption spectra of the v = 1-0 band of N_2 were measured using a Fourier-transform infrared spectrometer (FTIR) coupled to a unique 80-meter coolable high-pressure multipass cell, built previously with NASA support. Theoretical efforts at interpreting this spectra have been undertaken to understand the fine structure observed in the band profile. These measurements are now being extended to the v = 1-0 collision-induced absorption band of O_2.

In collaboration with L. Strow and D. Tobin (University of Maryland) the continuum absorption spectra of water vapor in N_2 and O_2 between 1000 and 2200 cm^{-1} was examined at a resolution of 0.04 cm^{-1} over a range of temperatures and pressures using the FTIR spectrometer and multipass cell discussed above. Preliminary analysis of the data suggests that may of the water transitions display super Lorentzian linewidths.

Infrared spectra of HFC134a (1,1,1,2-tetrafluoroethane), HFC134 (1,1,2,2-tetrafluoroethane), HFC143 (1,1,2-trifluoroethane), and HFC152 (1,2-difluoroethane) have been measured in the 10 μm region at 2 Mhz resolution using a tunable microwave-sideband CO_2 laser and an electric-resonance optothermal spectrometer (EROS). Microwave-infrared double resonance and precise ground-state combination differences lead to definite rotational assignments of the infrared spectra and unambiguous determination of the symmetries of the normal modes. For HFC134a, which is already in use in car air conditioners, the present results correct several previous vibrational misassignments established in lower resolution studies. FTIR investigations in collaboration with M. Crawford (DuPont) have been used to determine accurate integrated band strengths for the normal mode vibrations.

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A Facility for High Resolution Spectroscopy: Laboratory and Ground-Based Observations in Support of Upper Atmospheric Research

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Research Objectives

This research task consists of operating a spectrographic facility in support of upper atmospheric research that exploit the unique capabilities of the McMath-Pierce Fourier transform spectrometer (FTS). The facility responds to the needs and interests of the visiting NASA investigators working in the general field of upper atmospheric research. The research objectives have been related to either laboratory studies that produce line parameters required for the radiative transfer calculations needed to interpret remote sensing data or to ground-based atmospheric data recorded utilizing the McMath-Pierce Solar telescope. The FTS on Kitt Peak combines high spectral resolution (0.0056 cm^{-1} at 10 μm, 0.011 cm^{-1} at 3 μm) with expansive spectral coverage (600-30000 cm^{-1}), wide bandpasses (3000 cm^{-1}), high signal to noise ratios (300:1 to 1000:1) and short integration times (generally one hour or less). Line parameters obtained from the FTS spectra are typically accurate to 0.00005 cm^{-1} for line positions, and ±3% for intensities and line widths. The archive of atmospheric spectra produced by the McMath-Pierce FTS now covers almost two decades.

Summary of Progress and Results

Recent studies at Langley Research Center have focused on three important atmospheric gases, chlorofluorocarbon-22 ($CHClF_2$), carbon monoxide (CO), and ozone (O_3). The Kitt Peak measurements show an exponential increase rate in the CFC-22 total column of (7.0±0.2)% per year between 1980 and 1992. The CO content in two layers, up to 400 mbar and from 400 mbar to the top of the atmosphere, has been retrieved from Kitt Peak IR solar spectra. The measurements show an

asymmetrical seasonal cycle in both layers with a spring maximum and a late summer minimum. A technique has also been developed for retrieving O_3 amounts in four layers from Kitt Peak solar spectra. Total O_3 columns retrieved from the spectra show good agreement with TOMS satellite measurements.

The FTS was used in its double-passed (0.0025 cm^{-1} resolution) mode to record high-quality laboratory spectra of O_3 in the 10 μm region. Spectra of O_3 were also recorded using a glass multipass cell to provide line positions and relative intensities in numerous weaker bands from 2 to 13 μm. Analysis of FTS spectra produced the first determination of O_3 air-broadening and shift coefficients in the 13 μm region.

Crossed-path cells and a UV absorption system were used to monitor the O_3 amounts in the cells to allow the determination of absolute line intensities in the 10 μm region. Preliminary results were compared with those from Jet Propulsion Laboratory (JPL) and U. Reims (France).

Continuing analysis of CO_2 spectra has resulted in significant improvement in line positions and intensities in the 2.7 μm region (HALOE pressure-sensing channel). Laboratory spectra of CH_4 in a range of pressures bracketing that of the HALOE instrument cell were also recorded.

At JPL, line width and shape studies are being done for H_2O, CH_4, NO, NH_3, CH_3Cl, and H_2S. These efforts have been facilitated by the improvements done at the FTS to create an evacuated optical path between the absorption cells and the other components. Line mixing in foreign- and self-broadened water has been observed for the first time. The instrument can now be used to study line mixing in CO_2 as well. The widths and pressure-induced shifts of water lines in the 5 to 16 μm region are being extensively measured for air- and N_2- broadening.

The infrared laboratory program at Goddard continued its studies of the spectra of molecules of atmospheric importance using the FTS in both its single- and double- passed modes. The spectra of numerous species have been recorded and analyzed. These have included C_2H_6, C_3H_8, C_3H_4 (allene & methyl acetylene), CH_4, NH_3, C_2H_2, SiH_4, and the quadrapole spectra of H_2, D_2, HD, and N_2. These studies have produced molecular line parameters atlases and inputs to molecular line databases which are used by the atmospheric modeling and spectroscopy communities.

Spectra were obtained of helium and N_2 pressure broadened/shifted lines of C_2H_2 and of N_2O. A new KCl beamsplitter was used in these studies that produced usable spectra at wavenumbers as low as 480 cm^{-1}. The N_2O data were used to obtain intensities for lines near 17 μm. Dipole moments, band strengths and Herman-Wallis coefficients were determined from a complete analysis including effects of l-resonance. The analysis was part of a comparative study using the McMath-Pierce FTS and the high-resolution FTS at the National Research Council in Ottawa. The two spectrometers' intensities agreed to better that 1%, and no corrections for unbalanced thermal emission were required when the McMath-Pierce FTS was used in the dual-input mode with uncooled inputs.

All of the spectra obtained by the FTS for this program are now stored in an on-line CD-ROM jukebox that is accessible via the Internet. A proposal to NASA has been accepted designating Kitt Peak as an official complementary site for the Network for the Detection of Stratospheric Change (NDSC). Kitt Peak atmospheric measurements will be included in the NDSC archive.

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Atomic and Molecular Frequency Calibration

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Research Objectives

The objectives of this work were to select well behaved molecules and atoms, and then use frequency metrology based heterodyne frequency measurements on selected transitions in order to provide the basis for calculation of accurate frequency/wavenumber values for the portion of the spectra from 500 to 5000 cm^{-1}. This work involved the use of lead salt tunable diode lasers (TDLs) and a CO laser as a transfer oscillator. The measurements were referred to CO_2 stabilized laser frequency standards and provide wavelength/frequency calibration references with high precision. A milestone was reached with the publication in 1992 of NIST Special Publication 821. Subsequent objectives were to increase the accuracy of measurements by sub-Doppler techniques where possible, to extend the range of accurate frequency measurements to higher frequencies and to meld the NIST external cavity technology in the visible and near infrared with the mid infrared lead salt TDLs.

Summary of Progress and Results

(Progress period is for FY 1994 only, due to termination of the program with end of NASA funding). Advancing technology has lead to better FTS systems and the need for more accurate calibration frequencies for molecular transitions. This need can be met with sub-Doppler frequency measurements. Our first NIST sub-Doppler measurements on OCS were made with a CO v = 2 flowing-gas liquid-nitrogen laser. Polarization spectroscopic techniques utilizing heterodyne detection were used to provide the discriminant for locking the CO laser to the OCS sub-Doppler feature. As usual, our CO_2 laser frequency synthesizer was used to measure the CO laser frequency [Dax *et al.* 1994]. In this process one is limited to accidental overlaps (or near overlaps, i.e., reachable with an AOM) of CO and OCS, hence a limited number of measurements are possible. We also converted the CO laser to normal operation and attempted (with some success) OCS measurements in the 6 μm region [Dax *et al.*, 1995]. These measurements combined with those of our colleagues in Bonn have been included in a computerized update of NIST SP 821, which is currently available on the world wide web (address on world wide web is: http://physics.nist.gov/PhysRefData/.wavenum/html/contents.html).

In the post NASA funding era, we will rely on our colleagues who have incorporated sidebands on the CO laser for additional sub-Doppler measurements. At NIST, we have concentrated our efforts to bridge the gap across the 3.3 μm region to the near IR and the visible and have had some

success in scheme which divides the 1.06 μm Nd:Yag laser frequency by 3. This was done with our CO v=2 laser. A new more powerful laser has been constructed and a new power supply has been purchased for use with it. Our efforts to improve the utility of the lead salt TDLs have also continued, especially with our Bonn collaborators [Mürtz *et al.*, 1995]. Dr. Mürtz has spent half a year here in NIST continuing our efforts in this direction by investigating coatings and external cavity operation of the 3.3 μm TDLs.

Publications

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Calibration Facilities for NASA at SURF II

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Research Objectives

It is critically important to have a common radiometric base for the wide range of scientific missions being carried out by rocket, by satellite, and on the space shuttle. It has been demonstrated that this can be achieved by using the NASA Spectrometer Calibration Facility at SURF II, the Synchrotron Ultraviolet Radiation Facility at the National Institute of Standards and Technology. This beamline, with its large spectrometer calibration chamber, utilizes the calculable nature of synchrotron radiation to calibrate a wide range of spectrometer and photometer systems, thereby serving as a common radiometric base. The accuracy of this calibration source has been thoroughly documented and is adequate to this task.

Summary of Progress and Results

Thirty-five NASA related calibrations were performed at the NASA/SURF Spectrometer Calibration Facility at NIST during the period from 1994 through 1996. Users of the facility included: M. VanHoosier (two calibrations), NRL (SUSIM-ATLAS 3); T. Woods (fifteen calibrations), NCAR/HAO (EUV Solar Irradiance Experiment, Calibration and Test Equipment 3, and EUV Grating Spectrograph); R. Thomas (eight calibrations), GSFC (grating calibrations); R. Canfield (six calibrations), NIST (Dual Grating Monochromator for Diode Calibrations); and D. Judge (four calibrations), USC/SSC (Solar EUV Monitor and Solar EUV Hitchhiker). There have been a number of improvements to the facility during this period. The magnetic field monitoring and calibration system were upgraded. The energy of the electrons in the storage ring is determined by the magnetic field measurement. Vacuum system components were added to improve pumping and old hardware was replaced. Lighting and power connections were upgraded at the facility. Motion control hardware was improved and new computer programs were written for the motion control system. The gimbals system used to mount instruments inside the large vacuum chamber was improved.

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Diode Laser Spectroscopy and Instrument Development

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Research Objectives

The Diode Laser Spectroscopy and Instrument Development task consists of two primary efforts: development and deployment of near-infrared (1-4 μm) tunable diode laser (TDL) spectrometers for *in-situ* atmospheric gas sensing, and the laboratory acquisition and analysis of molecular spectral parameters require for interpretation of diode laser field spectra. Development of improved algorithms for data processing and autonomous spectrometer operation is also an important component of the research program. As part of a collaborative effort with the Center for Space Microelectronics at JPL, development and characterization of new near-room temperature laser devices for earth and space gas sensing applications is also pursued actively. This collaboration has resulted in the development of two lightweight, aircraft-borne spectrometers for measurements of water vapor and other gases from the NASA ER-2 and NCAR WB57F high-altitude research aircraft.

Summary of Progress and Results

During the past three years, the focus of this task has shifted from primarily laboratory measurements of spectral line parameters to the design, build, and deployment of new, lightweight TDL spectrometers operating in the 1 to 2 μm region. However, the laboratory measurement program has continued throughout the period and measurements were completed for three different molecules which lacked sufficient data for quantitative interpretation of balloon and shuttle (ATMOS) data recorded using Fourier transform infrared (FTIR) instruments. A rotational analysis of the 803 cm^{-1} band of HO_2NO_2 was performed using a high-resolution (0.005 cm^{-1}) FTIR spectrum recorded at 220 K. This strong band has been observed in stratospheric spectra, and we had previously reported absolute absorption coefficients for the band for use in analysis of the spectra. Absorption coefficients were also measured over the temperature range 210 to 300 K for the 1397 cm^{-1} band of HO_2NO_2 from high-resolution (0.005 cm^{-1}) FTIR and TDL spectra recorded at JPL. This band is the only IR band of HO_2NO_2 other than the strong fundamental at 803 cm^{-1} with a potential for measurement in the stratosphere.

Air-broadening coefficients and their dependence on temperature were measured for the ν_3 band of CF_4 at 1284 cm^{-1} to improve the accuracy of volume mixing ratios extracted from ATMOS spectra. The ν_3 band is the most suitable for atmospheric detection of CF_4 and no previous air-broadening

measurements had been reported for this band. FTIR spectra of COF2 were recorded at JPL as part of a collaborative effort with professor Geoffrey Duxbury's group at Strathclyde University in Glasgow, Scotland. These data were used to refine molecular constants for the fundamental band, as well as the hot band and overtone lines present throughout this spectral region..

In FY 1992 we began working with the JPL Center for Space Microelectronics (CSMT) to develop spectroscopic-quality room-temperature TDLs for potential use on a new class of lightweight infrared spectrometers. These spectrometers were intended for future space applications, as well as for earth atmospheric measurements. Through internal JPL funding a prototype system was assembled using distributed feedback (DFB) single-mode TDLs fabricated at JPL. These lasers operated at temperatures up to 50°C, and were tailored for monitoring of H_2O at 1.37 μm, and CO_2 at 1.43 μm. Output powers were up to 25 mW. Laboratory studies were extremely successful, and with additional funds provided to this task by NASA's Upper Atmospheric Research Program ($69K in FY 1995 and $30K in FY 1996) two functionally identical aircraft instruments were built to measure stratospheric water vapor from the ER-2 and WB57F aircraft.

The NCAR WB57F program encountered some delays and first flights of the H_2O sensor are scheduled for September 1996. The ER-2 instrument participated in the most recent (July through August 1996) STRAT campaign out of NASA Ames and Hawaii, and a measurement precision for stratospheric water vapor was demonstrated that is approximately five times better than current Lyman-alpha spectrometers flying on the ER-2. However, some in-flight alignment problems were encountered requiring minor changes to the optical system, and additional structural heating capacity. These modifications are in progress, as well as construction of a portable calibration chamber. Water vapor intercomparison flights on the ER-2 are scheduled for September 1996.

Publications

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The Heat Budget, Coupling, and Photochemistry of the Stratosphere and Mesosphere

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Research Objectives

This research effort is primarily aimed at studying the heat budget of the stratosphere and mesosphere (15-95 km) using data from the sensors carried aboard the UARS and other satellites. The approach is to use advanced radiative transfer routines to calculate solar heating rates and infrared cooling rates using the satellite data. The net diabatic heating is calculated on a monthly zonal mean basis and the meridional velocity components, w* and v*, are computed. These computations are then to be compared with model calculations. Additional heating and cooling processes, and their impact on the thermal structure are also investigated.

Summary of Progress and Results

Stratospheric and Lower Mesospheric Heat Budget (15 to 65 km)

- We have concentrated our efforts on the time period from October 1991 through April 1993. There are no calculations for the May to June 1992 time period when the UARS was powered off. We have not carried out calculations beyond April 1993 because of lack of contemporaneous measurements of temperature, ozone, water vapor, and nitrogen dioxide, as sufficient spatial and temporal resolution, after that time.
- For this time frame (13 full months), we have computed:
  - Radiative cooling rates (K/day) for the infrared (0 to 3000 cm^{-1}) for CO_2, H_2O, and O_3
  - Solar heating (K/day) for the UV, visible, and near infrared O_2, O_3, NO_2, and CO_2
  - Net diabatic heating
  - Meridional circulations (v* and w*) and streamfunctions

- We have also computed the same parameters over the corresponding months from the 1978 through 1979 time period using data from the LIMS experiment.
- We have demonstrated that radiation absorbed by molecular oxygen in the atmospheric bands at 762 and 688 nm was an important source of heat in the lower mesosphere (~65 km). It contributes up to 15% of the total diabatic heating at that altitude.

Relevant publications: Mertens *et al.*, 1996; and Mlynczak and Marshall, 1996.

Upper Mesospheric Heat Budget (65 to 95 km)

- Re-evaluated recent laboratory-based determinations of the Einstein A-coefficient for spontaneous emission by molecular oxygen at 1.27 μm, the O_2 ($a^1\Delta_g$ -> $X^3\Sigma_g$) transition. Radiation emitted by the O_2 at this wavelength significantly reduces the heating efficiency of the Hartley band of ozone in the mesosphere. After this re-evaluation, we found that the two existing laboratory measurements of this transition probability were different by a factor of 1.75. Our work demonstrated significant changes in the heating efficiency (4% absolute, 11% relative) due to absorption of solar ultraviolet radiation by ozone in the mesosphere.
- We further considered the role that exothermic chemical reactions play in determining the thermal structure of the mesosphere. In particular, we addressed whether or not the reactions could be responsible for the 'thermal inversion layers' frequently observed in the middle mesosphere (~70 to 75 km). We concluded that there was not sufficient chemical energy to perturb the thermal structure at those altitudes and that the phenomena may be dynamical in origin.
- Through our research, it has become apparent that the UARS dataset is not sufficient for doing a thorough study of the mesosphere (65 to 95 km) heat budget. We have determined and reported the requisite measurements needed for such a study.

Relevant publications: Meriwether and Mlynczak, 1996; Mlynczak, 1995; and Mlynczak and Nesbitt, 1995.

Photochemistry and Related Research

- We have used HALOE observations of NO_x at sunrise and sunset to test consistency with model predictions. Our results show that the observed diurnal variations of these gases fit very well with expectation, mainly reflecting the formation of NO_3 and N_2O_5 at night.
- We have conducted an analysis of the uncertainty in ozone derived from measurements of the O_2 ($^1\Sigma$) molecular oxygen airglow at 762 nm. This proxy technique for inferring ozone is currently being undertaken by members of the HRDI science team. The inference requires accurate knowledge of numerous kinetic (e.g., quenching rates) and spectroscopic parameters. This work identified several key parameters which are not sufficiently well-known to permit accurate inference of ozone using this technique.
- We participated in a study of non-LTE emission by ozone and carbon dioxide in the 10 to 11 μm region as observed by the CLAES instrument. Our interaction involved calculating vibrational temperatures for the several transitions of ozone in that spectral region. The work has been submitted for publication.

Relevant publications: Mlynczak and Olander, 1995; Edwards *et al.*, 1995; and Nevison *et al.*, 1996.

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Determination of Spectroscopic Properties of Atmospheric Molecules from High-Resolution Vacuum Ultraviolet Cross Sections and Wavelength Measurements

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Research Objectives

The penetration of solar radiation into the Earth's atmosphere in the wavelength region 250 to 130 nm is controlled by O_2 absorption in the Herzberg bands, the Herzberg continuum, the Schumann-Runge (S-R) bands, and the S-R continuum. Part of the radiation is transmitted through these bands, deep into the atmosphere, where minor species such as NO are photodissociated. For accurate modeling of these important processes, the computations involving O_2 and minor species must be performed on a line-by-line basis. For most of the S-R bands, such measurements have been completed by using the grating spectrometer at CfA with resolution of 0.4 cm^{-1}. However, the linewidths of some molecular bands of interest to atmospheric science, in particular the S-R bands of O_2 for v'>12 and the NO bands, are close to their Doppler widths (i.e., ~0.12 cm^{-1} at 295 K). Absolute cross section measurements and comprehensive rotational assignments for the O_2 bands have been obtained by using the newly developed Fourier transform (FT) spectrometer at Imperial College, London with resolution up to 0.03 cm^{-1}.

Summary of Progress and Results

Absorption cross section measurements of Doppler limited spectra can be carried out by using a vacuum ultraviolet (VUV) Fourier transform (FT) spectrometer. Absorption measurements with a good *S/N* ratio require a bright background continuum and some limit to the bandwidth of light incident on the spectrometer. In order to be able to make such ultra high resolution VUV absorption cross section measurements, we moved the VUV FT spectrometer from Imperial College, London, UK to the Photon Factory, Japan, where synchrotron radiation and a suitable zero dispersion predisperser are available. The strong continuum is available with the limited bandwidths of 20 to 40 Å. We have obtained 23 data files on the S-R measurements covering the wavelength region 175 to 185 nm with resolution of 0.06 and 0.12 cm^{-1}. The analysis of the FT results is in progress.

Absorption cross sections of CO_2 have been measured at 195 K and 295 K in the wavelength region 118 to 178 nm by using the 3-m VUV spectrometer and synchrotron source as background light source. The results have been published in the *Journal of Quantitative Spectroscopy Radiation Transfer* [Yoshino *et al.*, 1996].

Absorption cross sections of H_2O have been measured at 295 K in the wavelength region 120 to 188 nm by using the 3-m VUV spectrometer and synchrotron source as background light source. The results are accepted for publication in *Journal Chemical Physics.*

The predissociation linewidths of vibrational levels of isotopic oxygen have been calculated taking into account the spin interactions of the $B^3\Sigma^-_g$ state with the $^5\Pi_u$, $^3\Sigma^+_u$, $^3\Pi_u$ and $^1\Pi_u$ states, and the rotational coupling with the $^3\Pi_u$ state. The results have been published in *Journal Chemical Physics* [Cheung *et al.*, 1995].

The absorption spectrum of O_2 at high temperature has been photographed with 6-m vacuum spectrograph at the CfA. The absorption spectrum of the hot S-R bands covered the wavelength region 179 to 211 nm. The assignments of the absorption lines have been competed. We obtained rotational term values and molecular constants of the ground state of O_2 for $\upsilon = 1 — 4$. The results have been published in *Journal of Molecular Spectroscopy* [Cheung *et al.*, 1996].

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Collisional Lineshapes and Molecular Beam Spectroscopy of Atmospheric Molecules

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Research Objectives

The purposes of this program are to study collisional lineshapes and to obtain molecular beam spectra of various atmospheric molecules of interest to the NASA UARS (Upper Atmosphere Research Satellite), ATMOS (Atmospheric Trace Molecule Spectroscopy) and HALOE (Halogen Occultation Experiment) projects. The pressure broadenings, shifts and line profiles are required for quantitative monitoring of the distribution of contaminant gases and for temperature sounding of the atmosphere. Many of the molecular species of interest exhibit marked deviations in lineshape from the simple Lorentzian or Voigt profiles usually employed to model the spectral absorptions. A number of physical phenomena contribute to these lineshape distortions including collisional (Dicke) narrowing, speed-dependent collisional cross sections, non-impact (finite collision time) behavior, and collisional interferences (line coupling or line mixing). The precise measurement of these line profiles requires very high resolution infrared instrumentation such as the tunable difference-frequency-laser system and the color-center-laser photoacoustic spectrometer at NIST. Some of the heavier atmospheric molecules exhibit extremely dense, often strongly perturbed, spectra at normal atmospheric temperatures which have not been analyzed even with Doppler-limited resolution. In these cases molecular beam techniques can provide initial assignments due to sub-Doppler resolution and the considerable spectral simplification from the very low effective temperatures in an adiabatic expansion.

Summary of Progress and Results

- *Asymmetric Collisional Lineshapes in HF:* In a difference-frequency laser study of collisional broadening in the fundamental band of HF by Ar for comparison to "exact" quantum mechanical scattering cross section calculations, we observed an asymmetric lineshape at intermediate pressures (3-30 kPa). The magnitude and sense of the asymmetry could be attributed to correlations between velocity- and phase-changing collisions affecting the Dicke-narrowing profile for strongly shifted lines. The broadenings and shifts as a function of J were in excellent quantitative agreement with the quantum predictions based on a very realistic intermolecular potential.
- *Line Mixing and Pressure Broadening in Methane:* In an earlier study of pressure broadening in the congested Q branch of the C-H stretching fundamental band of methane, we found that the lineshape fits deteriorated and became unstable at pressures well below an atmosphere.

Therefore, we recorded the more isolated P and R branch multiplets using a difference-frequency spectrometer in order to assess the role of line mixing or collisional interference between the transitions with a common J value. With line mixing included, we were able to fit the spectra to an atmosphere, provided that we constrained the mixing among only transitions of a single tetrahedral symmetry species and imposed a zero sum rule on the mixing coefficients for each species. Nonlinearities vs. pressure for the mixing and shift parameters are observed since the Rosenkranz first-order perturbation conditions are exceeded for many blended lines at higher pressures.

- *Near and Far-Infrared Spectra of SO_2:* Doppler-limited spectra of several combination and overtone bands of SO_2 have been recorded with the difference-frequency laser to obtain improved anharmonic constants and for identification of species in planetary atmospheres. The strong $\nu_1+\nu_3$ band at 4 μm is in a clear atmospheric window and has been carefully evaluated for quantitative atmospheric monitoring. A new visible-to-far-infrared photomixing converter has been developed for terahertz frequency spectroscopy of atmospheric in the submillimeter wavelength regime. Self-broadening coefficients have been measured for several Q subbranches in the pure rotational band of SO_2, aided by the reduced congestion afforded by the extremely narrow Doppler width at these low frequencies.
- *Low Temperature Doppler-Limited Spectra of CF_4 and C_4H_6:* The heavy CF_4 and long dimethylacetylene molecules of minor atmospheric interest have been studied at low temperatures using a difference-frequency laser in order to understand their extremely complex spectra. The very strong $2\nu_3$ overtone in CF_4 has been recorded at T = 77 K and successfully analyzed as has been (at T = 195 K) the perpendicular ν_9 C-H stretch of dimethylacetylene which exhibits nearly free internal rotation.
- *Sub-Doppler and Air Broadening of Ethane Q Branches:* The $^rQ_0$ and $^pQ_3$ subbranches of the ν_7 perpendicular C-H stretching band of C_2H_6 are anomalously shaped but too congested to be resolved at the Doppler limit. However, they are relatively strong and are free of methane interferences, so are used for atmospheric signatures of ethane. We have resolved the rotational and torsional fine structure of these Q branches using sub-Doppler color-center laser excitation in an optothermal molecular beam apparatus to obtain predictive models of the temperature dependence of the Q branch profiles. Air broadening studies of these Q branches demonstrate that a simple average broadening coefficient with an linear inverse temperature dependence yields a simple accurate atmospheric lineshape model.

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Analysis of ATMOS Spectra for Trace Gases

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Research Objectives

The objective of this work is the comprehensive analysis of high-resolution atmospheric spectra recorded in the mid-IR by the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier transform spectrometer (FTS) during the Spacelab 3, Atmospheric Laboratory for Applications and Science (ATLAS) 1, (ATLAS) 2, and (ATLAS) 3 shuttle missions. Major objectives of this research are the retrieval of stratospheric and upper tropospheric concentration profiles of key trace gases from the ATMOS spectra and the calculation of updated line parameters for improved retrievals.

Summary of Progress and Results

Simultaneous stratospheric N_2O_5 and HNO_3 profiles at sunrise between 25°N and 15°S latitude and profiles of HNO_3 profiles at sunset between 42°S and 53°S latitude have been derived from the ATMOS/ATLAS 1 spectra recorded 9-1/2 months after the eruption of the Mt. Pinatubo volcano [Rinsland *et al.*, 1994a]. The measured HNO_3 volume mixing ratios (VMRs) are higher at all altitudes and latitudes than corresponding values measured by the Limb Infrared Monitor of the Stratosphere (LIMS) instrument during the same season in 1979, when the aerosol loading was near background levels. The largest relative increase in the HNO_3 VMR occurred near the equator at 30 km altitude where the ATMOS values are about a factor of 2 higher than the LIMS measurements. Two-dimensional model calculations show that the increase in HNO_3 and the ATMOS measurement of a steep decrease in the N_2O_5 VMR below 30 km can be explained by the enhanced conversion of N_2O_5 to HNO_3 on the surfaces of the Mt. Pinatubo sulfate aerosols. The results demonstrate the global impact of the $N_2O_5+H_2O \rightarrow 2HNO_3$ heterogeneous reaction in altering stratospheric odd nitrogen after a major volcanic eruption.

Measurements of the wavelength dependence of aerosol extinction in the 750-3400-cm^{-1} spectral region have been derived from the ATMOS/ATLAS 1 spectra [Rinsland *et al.*, 1994b]. Strong, broad aerosol features have been identified near 900, 1060, 1190, 1720, and 2900 cm^{-1} below a tangent height of ~30 km. Aerosol extinction measurements from ~0.05-cm^{-1} wide microwindows nearly free of telluric line absorption in the ATMOS spectra have been compared with transmission calculations derived from aerosol size distribution profiles retrieved from correlative SAGE (Stratospheric Aerosol and Gas Experiment) II visible and near infrared extinction measurements, seasonal and zonally averaged H_2SO_4 aerosol weight percentage profiles, and published sulfuric

acid optical constants derived from room temperature laboratory measurements. The calculated shapes and positions of the aerosol features are generally consistent with the observations, thereby confirming that the aerosols are predominantly concentrated H_2SO_4-H_2O droplets, but there are significant differences between the measured and calculated wavelength dependences of the aerosol extinction. We attribute these discrepancies as mostly due to errors in the low temperature H_2SO_4-H_2O optical constants, which we calculated from published room temperature values and the Lorentz-Lorenz relation.

For the first time, $ClONO_2$ profiles have been retrieved with a line list based on a quantum mechanical calculation [Rinsland *et al.*, 1994c]. The new parameters were used to retrieve $ClONO_2$ profiles from 7 sunrise and 7 sunset occultations recorded during the ATLAS 1 mission [Rinsland *et al.*, 1994c]. The new list produces slightly better fittings to the ATMOS spectra than previous parameters, both near the peak of the $ClONO_2$ Q branch where more absorption is now predicted and in the low wavenumber wing of the Q branch where less absorption is now predicted. The individual profiles, accurate to about ±20%, have been compared with previous observations and model calculations.

ATLAS 2 profiles of hydrogen chloride (HCl) and simultaneous profiles of chlorine nitrate ($ClONO_2$) and CFC-12 (CCl_2F_2) have been derived for examples of in- and out-of-vortex conditions [Rinsland *et al.*, 1995a]. Increased $ClONO_2$ VMRs are measured in the vortex below 20 mb (~25 km altitude) with a peak $ClONO_2$ VMR of 2.05 ± 0.45 ppbv (10^{-9} per volume) at 56 mb (~19 km altitude). Simultaneous CCl_2F_2 and N_2O measurements, combined with published empirical relations, indicate that only 0.28 ± 0.1 ppbv, about 10% of total chlorine, was bound in organic species at the $ClONO_2$ VMR peak in the vortex. A collocated vortex profile of HCl, referenced to simultaneous N_2O VMR measurements, has been used to derive an HCl mixing ratio of 1.21 ± 0.12 ppbv corresponding to the $ClONO_2$ VMR peak. The internal consistency of the ATMOS measurements is demonstrated by the agreement between the total chlorine mixing ratio of 3.62 ± 0.64 ppbv derived at the $ClONO_2$ VMR peak in the vortex and HCl measurements of 3.37 ± 0.37 and 3.76 ± 0.41 ppbv at 0.56 mb, where HCl is the only significant chlorine-bearing molecule. Outside of the vortex, the mixing ratio of HCl exceeds the mixing ratio of $ClONO_2$ throughout the stratosphere.

Absorption lines of stratospheric sulfur dioxide (SO_2) have been identified in the ATMOS/ATLAS 1 spectra [Rinsland *et al.*, 1995b]. Based on their analysis, a mixing ratio profile of SO_2 increasing from (13±4) pptv (10^{-12} by volume) at 16 mbar (~28 km) to 455±90 pptv at 0.63 mbar (~52 km) has been measured with no significant profile differences between 20°N and 60°S latitude. The increase in the SO_2 mixing ratios with altitude indicates the presence of a source of SO_2 in the upper stratosphere. Profiles retrieved from ATMOS spectra recorded during shuttle flights in April to May 1985 and April 1993 show similar vertical distributions but lower concentrations. Two-dimensional model calculations with SO_2 assumed as the end product of H_2SO_4 photolysis produce SO_2 profiles consistent with the ATMOS measurements to within about a factor of 2.

Elevated lower stratospheric HCl mixing ratios with a peak of ~2.9 ppbv, 10^{-9} parts per volume) near 500 K potential temperature (~19 km), were measured inside November 1994 Antarctic vortex [Rinsland *et al.*, 1996a]. The high HCl at low O_3 results from chemical production of HCl via the reaction of enhanced Cl with CH_4, limited production of $ClONO_2$, and the descent of inorganic chlorine from higher altitudes. Maximum removal of NO_y due to sedimentation of polar

stratospheric clouds (PSCs) inside the vortex occurred at a potential temperature (θ) of 500 to 525 K (~20 km), where values were 5 times lower than measurements outside [Rinsland *et al.*, 1996b]. Maximum loss of H_2O+2CH_4 due to PSCs occurred in the vortex at 425-450 K, ~3 km lower than the peak NO_y loss. At that level, H_2O+2CH_4 VMRs inside the vortex were ~70% of corresponding values outside. Elevated NO_y VMRs were measured inside the vortex near 700 K. Recent model calculations indicate that this feature results from downward transport of elevated NO_y produced in the thermosphere and mesosphere.

ATMOS profiles of OCS, HCN, SF_6, and $CHClF_2$ (HCFC-22) measured near 30°N latitude during the Spacelab 3 (29 April through 6 May 1985) and ATLAS 3 (3-12 November 1994) have been used to derive the change in the concentration of each molecule in the lower stratosphere over this 9-1/2-year period [Rinsland *et al.*, 1996c]. Exponential rates of increase inferred for 1985 to 1994 from these comparisons are (0.1±0.4)% yr^{-1} for OCS, (1.0±1.0)% yr^{-1} for HCN, (8.0±0.7)% yr^{-1} for SF_6, and (8.0±1.0)% yr^{-1} for $CHClF_2$ (HCFC-22), 1 sigma.

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High-Resolution Spectroscopy to Support Atmospheric Measurements

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Research Objectives

Remote sensing experiments on numerous satellite and Space Shuttle missions have shown that space-based measurements of infrared absorption or emission can be used to accurately determine the concentrations and distributions of stratospheric gas species on a global scale.

Detailed knowledge of the molecular spectra of ozone and other infrared-active atmospheric species is also needed for accurate calculation of atmospheric heating and cooling rates in climate models. The objective of this research task is to improve knowledge of the infrared spectroscopic line parameters (positions, intensities, assignments, halfwidths, and pressure-induced shifts) of key atmospheric constituents through laboratory measurements.

The measurements are made using the McMath-Pierce Fourier transform spectrometer (FTS) facility of the National Solar Observatory on Kitt Peak and the infrared tunable diode laser (TDL) spectrometer at NASA Langley Research Center along with specialized sample cells, many of which were designed and constructed at NASA Langley. Data analysis is performed primarily at Langley Research Center, and the theoretical interpretation of the results is done in collaboration with investigators at several other institutions in the United States and France.

These studies have contributed to a number of major upgrades of the US Air Force Phillips Laboratory's HITRAN and other spectroscopic parameters databases with world-wide distribution.

Summary of Progress and Results

We have made significant progress in our analysis of low-temperature air-broadened and self-broadened ozone spectra in the 4- to 15-μm region recorded with the McMath-Pierce FTS and the NASA Langley coolable cell in 1990 and 1991. The spectra were analyzed using our recently-developed multi-spectrum nonlinear least-squares technique to determine the pressure-broadening and shift coefficients and their temperature-dependences for numerous ozone lines.

Analysis of the air-broadened spectra has resulted in the determination of ozone air-broadening and shift coefficients for nearly 400 previously unmeasured lines in the 9-μm region and the first determination of these coefficients for ozone in the 13-μm region. Work on the 5-μm region is in progress.

The McMath-Pierce FTS was set up in double-passed mode in late 1994 and early 1996 to record high-quality spectra of ozone in the 10-μm region. Additional spectra in this region were recorded using the TDL system at NASA Langley in 1995. Crossed-path sample cells and an ultraviolet absorption system were used to monitor the ozone amounts in the cells to allow the determination of absolute infrared line intensities. Preliminary results were compared with those of researchers from Jet Propulsion Laboratory and two laboratories in France, and additional work is in progress to resolve apparent discrepancies among the various laboratories.

High-abundance FTS spectra of ozone were recorded using a new glass multipass sample cell in 1994 to provide high-quality data on line positions and relative intensities in numerous weaker bands of ozone through out the region from 2 to 15 μm. In 1995 we also recorded laboratory spectra of methane in a range of conditions bracketing that of the methane cell of the Halogen Occultation Experiment (HALOE) instrument currently in orbit on the Upper Atmosphere Research Satellite (UARS). The data were significant for HALOE instrument performance studies.

Continuing analysis of carbon dioxide spectra recorded with the FTS in 1982 along with new spectra recorded in 1994 has resulted in significant improvement in positions and intensities of over 10,000 carbon dioxide spectral lines in the 2.7- to 4.3-μm region.

The results will be submitted for publication in the near future.

Publications

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Smith, M. A. H., V. M. Devi, D. C. Benner, and C. P. Rinsland, Temperature dependence of air-broadening and shift coefficients of O_3 lines in the ν_1 band, manuscript submitted to *J. Mol. Spectrosc.,* 1996.

Inelastic Collision Processes in Atmospheric Infrared Absorbers and Their Relation to Atmospheric Pressure Broadening

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Research Objectives

Many trace species of critical importance in atmospheric processes, such as ozone and methane, can be monitored by remote sensing of their infrared absorption and emission bands. Recovery of accurate column densities and mixing ratios from field measurements requires accurate knowledge of band parameters, *viz.*, assigned line frequencies, line intensities, and pressure-broadened linewidths. The last-named quantities are generally derived from line-broadening models which have been tested against only a limited experimental database. We have been using time-resolved infrared double-resonance spectroscopy to measure inelastic collision rates, which are a key component of broadening models. A pulsed infrared laser is used to prepare selected rovibrational levels of the species of interest; these are probed by a tunable semiconductor diode laser which provides the resolution necessary for resolution of energy-transfer processes at the state-to-state level. Results obtained for a large number of systems indicate that in many cases the first-order collision models used to account for rovibrational relaxation and collision broadening are inadequate to describe the inelastic processes in detail, particularly for large J and K changes in collisions. Measurements in methane using polarized infrared pump and probe beams have shown that elastic reorientation cannot be neglected in methane-methane collisions, and makes a significant contribution to the self-broadening coefficient. We are now using the spectroscopic selectivity and sensitivity of these methods to obtain information on reactive free radicals of interest in atmospheric processes. In one task, Frequency-Modulation (FM) spectroscopy is being developed as a sensitive tool for studying kinetics and energy transfer in free radicals. In a second set of experiments, pulsed excimer laser photolysis of Cl_2O, combined with chlorine atom detection by resonant atomic fluorescence, has been used to study photodissociation yields of Cl_2O and verify the mechanism proposed by Sander et al. at JPL. Both of these are described in greater detail below.

Summary of Progress and Results

Monitoring concentrations of methane, ozone, and other atmospheric trace gases, and locating their major sources, requires use of spectroscopic remote sensing, which in turn requires an accurate database of spectroscopic parameters for the species of interest, including line frequencies, line strengths, and collision-broadened line widths. The latter are usually calculated from models which only take account of inelastic collisions. However, collision-induced changes in the space-fixed body frame angular momentum projection of the momentum projection of the molecule occur in all systems, within limits imposed by the isotropy of the collision environment. The effect of such collisions on the relationship between inelastic energy-transfer rates and line widths is often neglected. Using the time-resolved infrared double-resonance technique, with a Raman-shifted Ti:sapphire tunable pump source, we have measured both state-to-state energy transfer and collision-induced depolarization in ground-state and vibrationally excited methane. The measurements show that, when compared with available infrared and Raman linebroadening measurements, estimates using only inelastic collision rates systematically underestimate the actual linewidths for the corresponding transitions. It seems clear that more robust collision-broadening models, which take account of both higher-order inelastic channels and of non-inelastic contributions to the linewidths, will be necessary to generate the arrays of linewidths needed for accurate determination of atmospheric trace species concentrations.

In order to resolve some outstanding questions concerning the photophysics of Cl_2O, we set up an experiment using pulsed laser photolysis to provide wavelength selectivity, and Cl atom detection using atomic resonance fluorescence, which improved the time and excitation energy resolution of the measurement. The experiment was carried out by Koji Tamura, a visitor from the Japan Atomic Energy Research Institute during 1994-1995. Dr. Tamura designed and constructed the apparatus during his stay here, with assistance from members of Professor Mario Molina's research group, and carried out a series of measurements before he returned to Japan. He is now completing analysis of the data; when that is done, we will prepare a short publication on the results.

Frequency modulation (FM) spectroscopy has been utilized as a sensitive linear absorption based technique in physical chemistry for many years. Its capability to reach, in principle, shot noise limited sensitivity has stimulated our interest and promoted our work on developing several new high sensitivity techniques: transient FM (TFM), pulse-amplified FM (PAFM) and a hybrid of PFM with external cavity-PFM-cavity ring down spectroscopy. Current laboratory work is directed at improving the sensitivity of TFM for the study of rovibrational energy and alignment transfer in free radicals.

Publications

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Infrared Laboratory Spectroscopy in Support of Stratospheric Measurements

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Research Objectives

The objective of this program of infrared laboratory spectroscopy is to support NASA-funded measurements of the upper atmosphere by providing accurate and complete knowledge of the required line parameters. This research also aids NASA funded tropospheric investigations such as EOS and NDSC. The accuracies needed are determined by the state-of-the-art technology being applied by such instruments as the ATMOS interferometer.

This laboratory program provides improvements and new data for the line parameters in two general categories:

- minor gases which produce infrared absorptions so strong that the lack of detailed knowledge of their parameters would interfere with the detection of other species in the atmosphere by interferometric or laser techniques.
- less abundant trace gases that are important for atmospheric monitoring such as HNO_3, C_2H_6, and CH_3C.

The molecules of the first category have absorptions over wide expanses of the atmospheric spectrum so that the compilation of accurate line parameters requires analysis of many vibration-rotation bands. When the line parameters of a molecule over a spectral region are compiled, these data are made available to the NASA-sponsored investigators and eventually to the HITRAN compilations.

Summary of Progress and Results

Our efforts have been focused on compiling accurate spectral parameters derived from laboratory measurements for use in the reduction of stratospheric data. A large portion of this compilation has already been used in the various analysis of ATMOS spectra obtained from Spacelab 3 and the Atlas Shuttle experiments. Listings of spectral parameters derived from our laboratory measurements which are presently available to NASA investigators include the following: N_2O (500-4100 cm^{-1}), CH_4 (1100-4700 cm^{-1}), NO_2 (1520-1660 cm^{-1}), HDO (1000-4400 cm^{-1}), CO_2 (1200-1400 cm^{-1}), and $H_2{}^{16}O$, $H_2{}^{17}O$, and $H_2{}^{18}O$ (900-4400 cm^{-1}).

During 1994, 1995, and 1996 line parameter lists were created for $H_2{}^{16}O$, $H_2{}^{17}O$, and $H_2{}^{18}O$ in the 800 to 4500 cm^{-1} region and N_2O in the 500 to 3600 cm^{-1} region. Data were obtained for water vapor from 590 cm^{-1} to 5600 cm^{-1}. The $H_2{}^{16}O$ spectra were obtained with absorption path lengths from 20 cm to 433 km and the data were taken with a Fourier Transform Spectrometer (FTS) at the Kitt Peak National Observatory (KPNO). Computer aided measurements of the low pressure spectra was completed and an analysis of the pure rotational line positions and strengths was performed. Additional data of air and N_2 broadened water vapor were also obtained of which these results are part of a continuing study. A successful theoretical perturbation model was developed at JPL which applies to the interacting water vapor bands in the 5-6 micron region and the ground state bands in the 2600 to 4600 cm^{-1} region.

These results will support measurements to be made with EOS/AIRS and TES instruments and will aid in ground-based observations made by instruments in the NDSC. Laboratory spectra were also obtained for very low pressure HNO_3 and measurements to determine line positions and strengths continues. The results from the HNO_3 study will be used to resolve systematic biases in retrieved profiles of HNO_3 from ATMOS data and will have application with other infrared remote sensing measurements (e.g., UARS and CLAES).

Publications

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Laboratory Spectroscopic Measurements Relevant to Upper Atmospheric Research

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Research Objectives

Infrared spectroscopic data, which are needed in remote sensing and global warming studies, are obtained in the laboratory for several atmospheric trace gases including N_2O, CH_4, NH_3, SF_6, CCl_4, CFCs and HCFCs. The data are obtained by employing a high-resolution Fourier-transform spectrometer, cryogenically cooled absorption cells at pressures and temperatures representative of the various existing models of the atmosphere, and spectral resolution that is either comparable to or is significantly higher than that of the infrared instruments currently used in atmospheric remote sensing missions such as ATLAS/ATMOS and ADEOS.

Summary of Progress and Results

We have measured spectral absorption coefficients, which are also known as absorption cross-sections, k_ν ($cm^{-1}atm^{-1}$), of CFC-11, CFC-12, HCFC-22, SF_6, CF_4, and CCl_4 in their strongest absorption bands situated in the thermal infrared, since these bands are detected in the atmospheric spectra. The data were measured using a Bruker IFS120-HR Fourier-transform spectrometer and spectral resolution between 0.005 and 0.03 cm^{-1}, which is equal to or higher than what is used in most of NASA's satellite missions and field experiments. We have also measured N_2 -, O_2 -, and air-broadened line widths and line intensities in the ν_3 -fundamental band of N_2O at 4.5 μm and the ν_2 - fundamental bands of $^{14}NH_3$ and $^{15}NH_3$ at 10 μm at 200, 255, and 255 K. Using these data we have been able to deduce the temperature dependence of the line widths. The highly accurate absorption cross-sections have been measured at temperatures between 180 and 300 K. The measured absorption cross-sections are free from instrumental distortion, since the spectra were recorded under spectral resolution that was sufficiently high at the broadening pressures corresponding to tropospheric and stratospheric layers. Our data were obtained using N_2 as the broadening gas at pressures and temperatures given in commonly tabulated atmospheric models and represent tangent heights in solar occultation type remote-sensing observations of the atmosphere, and have been extended to cover also the conditions encountered in the atmosphere at Arctic and Antarctic latitudes. Our cross-section data have not only been incorporated into the established spectroscopic databases such as HITRAN and GEISA but have also been used by the science teams of several atmospheric satellite experiments such as UARS, ATMOS, MIPAS, and ILAS (of ADEOS).

Publications

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MODELING AND DATA ANALYSIS

A. STRATOSPHERIC DYNAMICS AND RELATED ANALYSIS
B. ATMOSPHERIC CHEMISTRY ANALYSIS AND RELATED MODELING
C. GLOBAL CHEMICAL MODELING

A. Stratospheric Dynamics and Related Analysis

Mountain Wave Theory and Observations

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Research Objectives

We plan to continue the analysis of ER-2 data initiated under this contract, and to extend our investigation to other upper tropospheric and lower stratospheric datasets. A proposal to support this work was submitted in response to NASA NRA-96-MTPE-02. We propose to analyze the variability in meteorological and trace gas mixing ratio data using statistical tools recently adapted from turbulence research. These techniques may shed light on the differences in the mechanisms responsible for tracer variability as opposed to those producing wind and temperature variability. We will also combine an advanced wave ray-tracing model [Eckermann and Marks, *1996 Adv. Space Res.* (in press)] with our mountain wave forecasting model to assess the potential for "remote" orographic forcing of variability, as well as other time dependent, 3-D, nonhydrostatic effects in mountain wave dynamics.

Summary of Progress and Results

The research performed under this task focused primarily on analyzing mesoscale variability (lengthscale < 1000 km) observed in the lower stratosphere. The initial emphasis of the work was on examining the role of orographically forced gravity waves (mountain waves) in the lower stratosphere. However, our work led to more general conclusions about mesoscale variability in this part of the atmosphere. Three of our most significant results are described below.

- Small scale variability in winds and temperature is gravity wave (although not necessarily mountain wave) dominated. This was shown by compiling ER-2 measured kinetic energy and potential energy horizontal wavenumber spectra for the AASE II, SPADE, and ASHOE/MAESA campaigns. Using transformations based on linear gravity wave theory we were able to show that the ER-2 horizontal wavenumber spectra agreed well with *vertical* wavenumber-frequency spectra measured by atmospheric profilers. This is a strong argument that the motions measured by both the ER-2 and the profilers are gravity waves. This analysis is described in Bacmeister *et al.* [1996b].
- Tracer mixing ratio spectra in the lower stratosphere are different from the spectra of winds and temperature. They are generally flatter, implying more variability at small scales. Further analyses using wavelet transforms reveal deeper differences between the tracer variability and that of wind and temperature. Tracer fluctuations are more likely to occur in large but sparsely distributed events. Wind and temperature fluctuations are more evenly distributed. The

analysis of tracer power spectra is described in Bacmeister *et al.* [1996b] and the higher order analyses using wavelets is discussed in Bacmeister *et al.* [1996a].

- Large mountain waves are encountered in the stratosphere, even over modest obstacles. Our analyses of ER-2 data show clear examples of wave encounters over large mountains such as the Rockies, but also over low mountains such as the Notre Dame mountains of southern Quebec (height ~500 m). Furthermore, the location and amplitude of these waves can be reasonably well predicted using a simple wave model which was developed and refined during the course of this research. The model as well case studies of ER-2 mountain wave encounters is described in Bacmeister *et al.* [1994].

Theoretical studies of wave generation by obstacles were also conducted. These studies examined the influence of obstacle shape on the evolution of steady state flows under conditions for which approximate analytical solutions exist. A highly-accurate pseudo-spectral numerical model was used to examine the validity of these approximate solutions. It was found that for steep topography, steady state flows does not result, even for assymptotically steady boundary conditions. Rather, an internally driven periodic solution develops, which is associated with slowly moving gravity waves forced by the obstacle. This work is described in Rottman *et al.* [1996].

Remaining Questions

While it seems likely that gravity waves are the dominant cause of mesoscale wind and temperature fluctuations in the stratosphere, the dominant sources of these waves are still not known. Orography can produce large individual wave events, however, there is gravity wave activity over ocean as well as over land. It is not yet clear whether other tropospheric sources, such as convection, are producing this background, or whether this background is produced *in situ* by some process.

Our analysis of the ER-2 data revealed dissimilarities between tracer variability and wind and temperature variability that go beyond simple differences in power spectral shapes, e.g., trace gas variability is more intermittent than that of wind and temperature. These differences may imply different dominant mechanisms for producing tracer vs. wind and temperature fluctuations. For example mesoscale tracer variability may contain large contributions from non-gravity wave motions, such as chaotic advection along isentropes, even though wind and temperature variability appear to be gravity wave dominated [Bacmeister *et al.*, 1996a, b].

Publications

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Over 15 oral or poster presentations based on this research were made, including an invited talk at the International Conference on Gravity Waves in the Atmosphere sponsored by the Canadian Network for Space Research, Lake Louise, Alberta, March 1994.

General Circulation Modeling of Stratospheric Dynamics and Transport

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Research Objectives

The objective of the proposed research is to increase our understanding of the complex interactions between chemistry, radiation, dynamics, and transport which determines the physical and chemical states of the atmosphere and their responses to perturbations. A series of modeling studies and comparison of the models with observations will be used to reach this objective. The primary tool used in this research will be the middle atmosphere version of the NCAR community climate model, version 2 (MACCM2), a 3-D general circulation model (GCM) which extends from the surface to the upper mesosphere. A mechanistic version of the model, in which the troposphere is replaced by a specified geopotential distribution near the tropopause, will also be used. Both versions of the model will be coupled to a moderately complex ozone chemistry model, initially to study the maintenance of the ozone distribution and subsequently to study the influence on the evolution of the circulation through changes in the radiative heating.

Summary of Progress and Results

This grant ended in August 1995 at which time significant progress had been on most of the principal objectives of this proposal as discussed below. This grant provided a relatively modest level of incremental funding to allow extensions of research which was largely funded by NSF, and by grants from other agencies, including NASA. While some of the research described here is primarily funded from other sources, much of it would not have taken place without the funds provided by this grant, and all of it is greatly aided by this funding.

Several long integrations of the middle atmosphere version of MACCM2 were completed to analyze its climatological behavior, the dependence of the simulation on horizontal resolution, its ability to simulate the distributions of long lived trace constituents. The basic climatology of the model was documented in Boville [1995]. The model simulates the annual cycle of the Northern Hemisphere circulation quite well but produces much too strong a polar vortex in the Southern Hemisphere. The Southern Hemisphere circulation was found to improve only slightly with resolution over the range from T42 to T106.

A 2-D model study [Garcia and Boville, 1994] demonstrated that the excessive strength of the Southern Hemisphere polar vortex in MACCM2 and other GCMs can be explained largely by an absence of gravity wave driving in the lower mesosphere.

The mechanistic version of the model was used to test new gravity wave parameterizations which are required to improve the simulation of the Southern Hemisphere polar vortex. This improvement is essential in order to allow reasonable simulations of transport and chemistry during austral winter. Following encouraging results in the mechanistic model, extensive testing was performed in the full GCM. Two types of parameterization were examined. The first is a variant of the Lindzen style scheme commonly used in 2D models [e.g., Holton, 1982; Garcia and Solomon, 1985; Hitchman and Brasseur, 1987] and the second is the simple parameterization of a gravity wave spectrum by Fritts and VanZandt [1993] and Fritts and Lu [1993]. Significant problems were identified with the Fritts and Lu parameterization and the later testing concentrated on the Lindzen style scheme. It was found that vastly improved simulations of the Southern Hemisphere vortex could be obtained by incorporating a suitable spectrum of gravity waves, although some problems with the seasonal evolution of the vortex remain. The MACCM2 circulation with the gravity spectrum parameterization included has been extensively used at NCAR and within the NASA HSRP program for off-line chemical transport experiments.

An off-line parcel trajectory model has been developed for MACCM2 and the mechanistic model. The parcel model uses similar trajectory and interpolation algorithms to the semi-Lagrange tracer transport algorithm in MACCM2 to advect an arbitrary list of Lagrangian parcels and to determine the model state variables at their locations. The parcel model can be run either on the MACCM2 hybrid sigma/pressure surfaces, or on potential temperature surfaces. Significant differences are found between parcel trajectories in the two coordinate systems, associated with small vertical structures in the GCM wind fields. These structures are related to the numerical formulation of the MACCM2 (which is similar to most other GCMs) and can produce rapid displacement of parcels across potential temperature surfaces without accompanying diabatic heating. This problem also affects continuous tracers in the GCM (such as water vapor) and is believed to explain the excessively rapid ascent and dispersion of the annual water vapor signal simulated by MACCM2 in the lower tropical stratosphere found by Mote *et al.* [1995]. These small structures have been almost eliminated in tests using 3-D semi-Lagrangian dynamics with monotonic interpolates.

An ozone chemistry model has been coupled into the MACCM2 and several multi-year simulations have been performed with a series of modifications to the chemical model. The model is able to reproduce many aspects of the observed distributions of ozone and other trace gases when the predicted ozone field is not used to compute the radiative heating rates. This work was published in Rasch *et al.* [1995].

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Observational and Model Studies of Large-Scale Mixing Processes in the Stratosphere

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Research Objectives

Research funded by this grant has focused on large-scale transport processes in the stratosphere. We used observational and modeling approaches to investigate the mixing of air between the interior and exterior of the polar vortices. The observational studies compared the evolution of observed tracer distributions with Lagrangian calculations from analyzed winds. The mixing of tracers by the large-scale, quasi-horizontal circulation was also investigated with a barotropic model to determine how important wave critical lines are in the mixing process. The mixing behaviors of the Northern and Southern Hemisphere polar vortices were compared to help understand the differences in ozone behavior between the hemispheres. The model was also used to study mixing in the mesosphere by the 4-day wave.

Summary of Progress and Results

Two papers describe observed large-scale mixing in the Antarctic and Arctic polar vortices, respectively [Bowman, 1993; Dahlberg and Bowman, 1994]. A short follow-up report was prepared showing transport statistics for the first two years of the UARS mission [Dahlberg and Bowman, 1995]. The first paper demonstrated that the Antarctic vortex is nearly completely isolated in the lower stratosphere until the vortex breaks down in late spring. The mixing is strongly height dependent in the lower stratosphere. In the Arctic there is more mixing than in the Antarctic, but the time scale for mass flow through the vortex is still longer than a season.

A numerical model was used to investigate mixing by barotropic instability, which is the probable origin of the 4-day wave in the upper stratosphere [Bowman and Chen, 1994]. Surprisingly, the model shows that even with unstable, growing waves on both flanks of the polar jet in the upper stratosphere (that is, both inside and outside the vortex), there is essentially no exchange of air between the interior and exterior of the vortex. Together with the earlier Total Ozone Mapping Spectrometer (TOMS) observational study [Bowman and Mangus, 1993], the numerical modeling experiments and the observational results in Bowman [1993] and Dahlberg and Bowman [1994, 1995] provide confirmation of the dynamical isolation of the polar vortices described by Hartmann *et al.* [1989], Schoeberl *et al.* [1989; 1992], and Schoeberl and Hartmann [1991].

The observational studies described above showed that the barriers around the polar vortices are strong. Within the surf zone, however, mixing is rapid and efficient. By using a simple stochastic

model it is possible to show that the randomizing effects of wavebreaking can lead to transport that statistically behaves like diffusion [Bowman, 1995].

With the existence of the polar mixing barriers firmly established, recent research has concentrated on understanding the cause of the mixing barriers, both those around the polar vortices and in the tropics. The results conclusively show that the mixing barriers around the polar vortices are a result of the lack of waves with critical lines near the jet cores [Bowman, 1996]. There are no critical lines in the jet core because there are no waves with fast phase speeds comparable to the speed of the jet. Since waves break near their critical lines, and mixing is due to wavebreaking, the absence of critical lines leads to a region of weak mixing. In the Arctic, large deformations of the polar vortex do lead to some ejection and entrainment of air across the vortex boundary [Plumb *et al.*, 1994; Waugh *et al.*, 1994; Dahlberg and Bowman, 1994, 1995]. The summer hemispheres are well mixed despite the weaker wave fields because the jets are weaker and waves have critical lines throughout the hemisphere.

We are now completing a study of the tropical mixing barriers that are evident in tracer data [e.g., Hitchman *et al.*, 1994; Grant *et al.*, 1996]. We have used output from the Geophysical Fluid Dynamics Laboratory (GFDL) SKYHI model to investigate the tropical mixing barriers at 450 K. Trajectory calculations show that the tropical barrier mechanism is similar to the one that produces the polar mixing barriers: localized jets have wind speeds greater than the phase speed of the extant waves. In the case of the polar mixing barriers, waves are propagating from a region of low wind speed to a region of high wind speed. As a result, the phase speeds of the waves are slower than the wind speed in the jet. In the case of the tropical barriers, waves are generally propagating from the mid-latitudes, where wind speeds are high, into the tropics, where they are low. As a result, they encounter critical lines and break before reaching deep into the tropics. Once again, a zone of weak mixing results from the absence of critical lines and wavebreaking. The tropical barriers in the model are generally more porous than the wintertime polar barriers. Two papers are submitted or in preparation on this subject [Bowman and Hu, 1996a, b].

Finally, in an observational study, Hollandsworth *et al.* [1995] describe the global structure of the Quasi-biennial Oscillation (QBO) in Solar Backscatter Ultraviolet Spectrometer (SBUV) ozone data.

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Advanced Methods for Data Assimilation

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Research Objectives

Data assimilation is the process of combining observations of a dynamical system with a computer model of the system, in order to obtain an ongoing best estimate of the evolving state of the system. Increasingly it is being recognized that employing data assimilation methods is likely to play a critical role in furthering scientific understanding of fundamental Earth System processes. While considerable research efforts directed toward the assimilation of meteorological data into atmospheric models have been underway for some time, relatively little attention has been devoted to the assimilation of atmospheric trace constituent data. The behavior of many trace constituents, such as ozone, carbon monoxide, and methane, is vitally important for climate processes. The objective of this research is to carry out a comprehensive study on the assimilation of atmospheric trace constituents, using data primarily from the Upper Atmosphere Research Satellite (UARS), and employing the rigorous, first-principles approach of estimation theory.

Summary of Progress and Results

One of the primary tools of estimation theory for data assimilation is the Kalman filter, which evolves both the dynamical variables (in our case constituent mixing ratios) and their spatial error correlations, and provides error bars on the assimilated data product as well, all at the resolution of the underlying dynamical model. Thus the Kalman filter differs considerably from so-called "Kalman mapping techniques" and other mapping techniques, which traditionally have been used to provide gridded fields from sparsely-observed data. Implementation of a Kalman filter for constituent data assimilation, while computationally expensive, provides a benchmark for studies in constituent data assimilation.

Using a two-dimensional transport model on isentropic surfaces, we have implemented a Kalman filter for assimilating data from several UARS instruments [Lyster (in press)]. Numerous computational obstacles were overcome in the development of this global Kalman filter data assimilation system, which runs only on massively parallel computers. The Kalman filter has been used to assimilate methane data from HALOE, a solar occultation instrument aboard UARS. Even though HALOE provides only about thirty profiles per day, the Kalman filter generates global maps which validate well against the more dense measurements of other instruments on the UARS platform [Menard, *JGR*]. Refinements currently underway include a method [Cohn, 1997] to account for the fact that constituent estimation errors tend to be lognormally- distributed, rather than Gaussian-distributed as is assumed in the standard Kalman filter, and a coordinate transformation [Cohn, 1993] to more accurately portray the constituent estimation error dynamics.

The success of the HALOE assimilation has motivated further research into assimilating SAGE data, with the goal of providing datasets with improved representation of lower stratospheric ozone.

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Assessment of DAO Stratospheric Product

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Research Objectives

This research effort is closely coordinated with the project headed by Dr. A. Douglass ("3-D Chemistry and Transport Model"). Both efforts are highly leveraged by the Data Assimilation Office (DAO), especially the use of computer resources and the production activities in support of AEAP field missions. The AEAP funding is to improve the long-term fidelity of the winds from the assimilation for use in transport studies and to produce datasets of one year duration or longer. The quality of the winds is evaluated by the transport applications that are validated with satellite, aircraft, and balloon observations, as well as by comparisons with other assimilation system products.

Summary of Progress and Results

Transport Evaluation: A series of assimilation experiments, GCM (general circulation model) experiments, and corresponding transport model runs have been completed for the month of December 1991. These results investigated several properties of the assimilation system and of transport modeling using assimilation produced winds. Results show that spatial smoothing of the analysis increments results in not only smoother horizontal transport, but smoother vertical transport as well. Smoothing of the assimilation analysis increments was also produced by the BIAU (Balanced Incremental Analysis Update) method with similar results. Studies were also made with varying vertical resolution in the transport model. Results show that the transport model has less vertical structure when run as closely as possible to the vertical resolution of the assimilation system.

Diagnostic Evaluation: Comparisons of diagnostic quantities, such as the mean residual circulation, were compared between the GSFC data assimilation system and the UKMO data assimilation system. The two systems were independently developed, but use essentially the same input observations. They showed excellent agreement for the mean winds and temperatures and basic vortex structure. Agreement was more qualitative for the secondary circulations, such as the residual circulation, as well as for details of the tropical wind fields. These comparisons highlight areas in which the assimilation systems may be improved.

GCM Evaluation: Work is being planned for evaluation of the stratospheric component of the DAO's GCM as part of GRIPS (GCM Reality Intercomparison Program for SPARC: Stratospheric Processes And their Role in Climate). As part of GRIPS, the DAO's GCM will join in a stratospheric climatology comparison with approximately twenty other stratospheric GCMs. A more accurate GCM climatology can improve the DAO's assimilation products.

Gravity Wave Drag: In conjunction with the DAO, work has begun on implementing a new gravity wave drag (GWD) scheme into the DAO's GCM. Improved GWD, when used in the data assimilation system, should improve the vertical motion field throughout the stratosphere, including the lowest stratospheric levels.

New Assimilation System: The DAO has recently begun testing of its newest assimilation system. This includes a new GCM (with additional vertical levels, new radiative transfer scheme, GWD, and a number of other improvements) and two new analysis schemes. Stratospheric diagnostics quantities have been calculated for an initial data assimilation experiment and a transport run is planned.

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Dynamical Meteorology of the Equatorial and Extratropical Stratosphere

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Research Objectives

An observational study of the dynamical meteorology of the equatorial and extratropical stratosphere was performed, emphasizing large-scale motions and their coupling with the underlying troposphere.

Summary of Progress and Results

In the extratropical Northern Hemisphere winter stratosphere, distinct circulation anomalies are attributable to the quasi-biennial oscillation of the equatorial lower stratosphere and a pattern resembling the North Atlantic oscillation of the polar winter troposphere. The influence of the QBO on planetary wave motions is seen primarily in the upper stratosphere, where a dipolar anomaly of wavedriving is found, causing the mid-latitude mean flow to be anomalously weak (strong) in QBO easterly (westerly) years. The lower stratosphere is more noticeably influenced by a tropospheric pattern containing elements of the North Atlantic oscillation, Siberian high, and Alaska blocking. These individual features, in combination, project significantly onto the zonally averaged flow of the polar upper troposphere and affect the ability of planetary waves to propagate vertically into the lower stratosphere. Lag correlations suggest that the effect is directed upwards, although recent modeling studies also indicate a possible downward influence of stratospheric circulation anomalies on the troposphere. Our analysis, at this stage, cannot exclude the latter possibility. Vertical coupling of this pattern occurs mainly on seasonal to interannual timescales. In a separate investigation, the coupling of weekly to intraseasonal anomalies (generally referred to as `low-frequency variability' among tropospheric dynamicists) was found to occur in spatially localized patterns indicative of Rossby wavetrains centered in geographical regions with frequent blocking activity (e.g., Alaska, Scandanavia, central Russia). The analysis technique utilized a new statistical tool developed by us, viz., rotated singular value decomposition (RSVD), to identify the most important vertically coupled patterns of poleward heat flux, corresponding to local regions of vertical propagation as measured by the generalized Eliassen-Palm flux. Several studies were also performed of tropical wave motions and mean flow oscillations (QBO and SAO). The horizontal structure and group propagation of disturbances over the western, central, and eastern Pacific was examined with gridded ECMWF analyses in conjunction with outgoing

longwave radiation (OLR) data. Contrasting properties of tropical depression disturbances in the convergence zones and antisymmetric Rossby-gravity waves centered about the equator were identified objectively with multivariate rotated principal component analysis. One particularly interesting discovery was the eastward group propagation of Rossby-gravity waves from the central to eastern Pacific, with apparent bifurcation of ray paths into the lower stratosphere and lower troposphere so as to avoid the eastern Pacific upper troposphere, where a separate type of Rossby-gravity wave is found having slightly lower frequency and shorter horizontal wavelength. Waves from the central Pacific are of convective origin while those in the eastern Pacific upper troposphere probably result from lateral forcing; this region contains a westerly `duct' due to the Walker circulation into which disturbances from extratropical latitudes may propagate. A separate study of near-equatorial convection revealed a common type of disturbance with eastward phase velocity of 10-13 m/s, sometimes embedded within, but generally unassociated with, the more familiar tropical intraseasonal oscillation (or Madden-Julian oscillation). Gridded analyses and rawinsonde data were used to elucidate the penetration of quasi-stationary monsoon circulations into the summer lower stratosphere. The role of gravity waves in the quasi-biennial oscillation was examined with a two-dimensional model using recent observations of apparent tropical upwelling in UARS water vapor measurements to infer a vertical profile of the Brewer-Dobson vertical mean motion near the equator. These results allowed an indirect estimate of gravity-wave fluxes required in conjunction with the observed large-scale Kelvin and Rossby-gravity waves to drive the QBO in the presence of mean upwelling. In a separate but related observational study performed in collaboration with Kaoru Sato of Kyoto University, direct and indirect estimates of vertical momentum flux associated with short-period disturbances (1 to 3 days) observed in Singapore rawinsonde data were obtained using a WKB formula derived by Dunkerton [1995 JMSJ] for the buoyancy flux of gravity waves in vertical shear. Rocketsonde data were used to investigate the climatology of stratopause and mesopause semiannual oscillations and evidence of coupling between the stratopause SAO and underlying quasi-biennial oscillation. The QBO modulates the descent of SAO westerlies, while new westerly phases of the QBO are initiated by the SAO. This mechanism acts to reset the QBO `clock' but is only one of several ways in which the QBO is affected by the seasonal cycle as its westerly and easterly phases descend. Finally, UARS constituent data in conjunction with UKMO analyses revealed an intermittent, latitudinally narrow mixing zone in the tropical upper stratosphere equatorwards of the subtropical jet which acts as an apparent barrier to isentropic mixing in late Northern Hemisphere winter.

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Dynamical and Chemical Studies of the Middle Atmosphere Using Satellite Data and a 2-D Model

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Research Objectives

The fundamental goal of this work is to improve our understanding of the dynamics and chemistry of the middle atmosphere through the use of satellite datasets and a two-dimensional numerical model. We proposed to carry out investigations in four different task areas involving tracer transport at low latitudes: 1) aerosols, ozone, water vapor and the quasi-biennial oscillation; 2) diagnosis of potential vorticity dilution and transport; 3) spatial variation in lower stratospheric circulation; and 4) long-term trends in tropical tropopause structure.

Summary of Progress and Results

This grant helped support two Ph.D. and 5 M.S. students to completion and led to 12 publications. Fundamental progress was made in understanding the nature of transport and dynamical processes. Specific findings include:

- significant geographical variation exists across the tropical lower stratosphere, tied to seasonal monsoon structures, which determine preferred longitude bands of transport into and out of the tropics;
- the Brewer-Dobson circulation includes a two-step process for entry of air into the stratosphere, first into a tropical reservoir, then detrainment into a lower or upper transport regime governed by the phase of the QBO and the annual cycle;
- the WISCAR model now has a QBO which may be driven analytically by three different methods, lending insight into QBO dynamics;
- the degree of inertial stability or instability plays an integral role in determining structure and transport in the tropics;
- observed gravity wave momentum fluxes are a primary component of the lower stratospheric momentum budget.

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Wave Dynamics and Transport in the Stratosphere

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Research Objectives

This grant supports a program of theoretical studies, numerical modeling, and data analysis designed to elucidate the dynamics of motions in the stratosphere and their role in the transport of heat, momentum, and trace chemical substances in the lower stratosphere, and across the tropopause. The emphasis of the project is on the following topics:

- Utilization of a numerical model of cumulonimbus convection to examine the transfer of momentum between the troposphere and stratosphere in connection with tropical convective storms.
- Use of the same model in an attempt to determine the role of high-frequency gravity waves generated by tropical convection in dehydration of the lower tropical stratosphere.
- A two-dimensional (zonally symmetric) model study of the comparative roles of non-local stratospheric forcing and tropospheric Hadley cell dynamics in the transport of mass across the tropical tropopause.
- Utilization of tracer transport models to study the seasonal and geographical variability in quasi-isentropic mass exchange across the extratropical tropopause.

Summary of Progress and Results

Characteristics of stratosphere-troposphere exchange in a general circulation model: Dr. Phil Mote utilized the NCAR global circulation model (CCM2) in an analysis of simulated stratosphere-troposphere exchange using idealized tracers and Lagrangian parcel trajectories. These revealed that while the magnitude and seasonal cycle of mass transfer through the tropical tropopause is approximately correct in the CCM2, many of the details are not very realistic, and the model does a relatively poor job of simulating the exchange of water vapor so that in its present state of development it is not a suitable tool for studying possible trends in stratospheric water vapor [Mote *et al.*, 1994].

Gravity wave dynamics: We have continued our studies of convectively generated gravity waves in the lower stratosphere using a two-dimensional nonhydrostatic model for cumulonimbus convection. Joan Alexander completed a study of the time-space Fourier spectra of gravity waves generated in a simulated extratropical squall line [Alexander *et al.,* 1995]. The depth of the diabatic heating within the storm was found to determine a dominant vertical wavelength in the gravity wave response. Her analyses enable us to better compare model results with published observational data from radar and aircraft measurements [Alexander and Pfister, 1995]. In another paper [Alexander, 1996] she combined the time-space Fourier analysis with a wavelet analysis in order to define wave packets, whose propagation can then be computed using ray tracing techniques. She used these analysis tools to evaluate the transmissivity of convectively generated waves, and to determine the levels at which various wave groups break in the upper stratosphere and mesosphere, and their impact on the momentum balance. The results suggest that a single large convective storm could provide a significant fraction of the zonal mean gravity wave forcing required to account for the instantaneous zonal mean momentum balance in the mesosphere.

Cross-isentropic mass flux in the stratosphere: In the extratropics the time and zonal mean air mass exchange across an isentropic surface in the stratosphere depends primarily on the zonal drag produced by eddy dissipation in the first few scale heights above that level. Since in the lower and middle extratropical stratosphere the eddy dissipation is primarily due to dissipating planetary and synoptic scale eddies, it is possible to utilize conventional climatological data to estimate the mean downward mass flow across a given isentropic surface in the extratropics in each hemisphere. The compensating upward mass flow in the tropics can then be estimated by mass continuity. Rosenlof [1995] used the UKMO stratospheric analyses available through the UARS project for the 1992-1993 period to compare the annual cycle in the meridional residual (mass) circulation determined directly from the UKMO data with that deduced by the "downward control" method, and with the diabatic circulation computed with the aid of a modern radiation code. The computed seasonal cycle shows, in agreement with other work, that the global mean cross-tropopause flux is nearly twice as great in Northern Hemisphere winter as in Southern Hemisphere winter, and that in the lower stratosphere descent in the Southern Hemisphere polar vortex is slower than in the Northern Hemisphere polar vortex.

Stratospheric dehydration: Dr. Brian Potter examined the possible role of tropical convective systems in contributing to dehydration of the tropical lower stratosphere. Potter developed a version of our cloud model that included fairly detailed representations of long- and short-wave radiation, ice phase cloud microphysics, and boundary layer transfer processes. He used this model to simulate the diurnal convection cycle in the Borneo region where topographic forcing and land-sea heating contrasts provide the low level moisture convergence that is required to initiate deep convection in the tropics. He compared the roles of convective scale motions and organized mesoscale circulations in providing irreversible transport from the troposphere to the stratosphere. The model simulations suggest that convectively-generated gravity waves may play an important role in dehydrating the tropical lower stratosphere. Vertical parcel displacements produced by gravity waves promote the formation of thin ice clouds in the lower stratosphere. Such clouds formed upwind of the convective region in all simulations where ice was allowed to form. It is concluded that thin cirrus clouds produced by gravity waves can contribute significantly to the formation and maintenance of the observed water vapor minimum in the lower tropical stratosphere.

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General Circulation of the Southern Hemisphere Stratosphere

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Research Objectives

The long-term goal of this project is to better understand the dynamical processes at work during the seasonal evolution of the southern stratosphere and the reasons for the interhemispheric differences in the stratospheric circulation. The methodology for research is based on two complementary lines of investigation. One line of investigation uses observational data to provide a three-dimensional (3-D) view of the evolving flows. The other line of investigation uses primitive-equation (PE), 3-D models of the atmosphere to perform simulations for selected periods and to carry out hypothesis-testing experiments.

Summary of Progress and Results

Variations in the Stratospheric Circulation: This investigation aims to gain insight into variations in the extratropical stratospheric circulation with emphasis on understanding observed interhemispheric differences. Many previous studies have attributed observed or modeled variations in the extratropical stratosphere to external factors (e.g., the quasi-biennial oscillation in equatorial zonal winds or variations in tropospheric planetary wave activity). Our approach consists of analyzing variations in middle atmosphere model simulations in which there are no such 'external' variations imposed are investigated. First, we analyze the interannual variability in simulations using a 3-D primitive-equation model of the middle atmosphere in which the prescribed boundary and radiative forcing are given by idealized fields without interannual variations. In each of the experiments with a large wave 1 amplitude (comparable to that observed in the Southern Hemisphere) imposed at the lower boundary, there is substantial interannual variability in the stratospheric winds and wave amplitudes during the late winter and spring seasons. The seasonal cycle and interannual variability of the simulated zonal winds and wave 1 amplitude are comparable to those observed in the Southern Hemisphere (SH) stratosphere. For even larger wave 1 amplitudes at the lower boundary, the simulated evolution of the zonal flow and wave 1 amplitude resembles more closely observed conditions in the Northern Hemisphere.

To gain a better understanding of the mechanisms producing the interannual variations in these simulations, we have been using a highly-truncated quasi-geostrophic model on a beta plane. The variations in stratospheric planetary wave amplitudes and zonal mean zonal wind in the presence of steady planetary waves in the troposphere have been examined through an analysis of the steady

solutions of the model as well as time integrations. The model can include the interactions of the zonal mean flow with planetary waves as well as the interactions of these waves with each other, and is thus an extension of that used in Yoden [1987]. The impacts on the results of adding a zonal wavenumber 1 component and one more meridional mode to the configuration used by Yoden (zonal mean and zonal wavenumber 2 only) have been investigated separately. In the experiments with the zonal wave 1 component added, three branches of steady solutions with different vertical structures are obtained. One of them is steady stable and has an intermediate value of the zonal mean wind, strong wave 1 amplitude and weak wave 2 amplitude; the corresponding solution branch in Yoden's study is unstable. The second solution is stable oscillatory and has a critical layer near 30 km, the third is unstable. In the experiments with two meridional modes, the range of wave 2 amplitude for which multiple steady solutions exists is narrower than in the experiment with only one meridional mode. In addition, the stable, oscillatory solution appears as a stable solution with a periodic (chaotic) variations of the zonal wind and wave amplitude. These results suggest that a rich variety of variations in the stratospheric circulation are possible even under constant 'external' conditions.

Transport Processes in the Southern Polar Stratosphere: In preparation for STRATEOLE, we have studied transport processes in connection with ozone variability in the wintertime Southern Hemisphere polar lower stratosphere. Chemistry in this region is such that ozone is mainly conserved on time scales of a few days, with sparse and localized chemical sources and sinks. The winter polar vortex strongly controls transport in the polar regions and dynamic processes can be approximately reconstructed by advecting air parcels along isentropic surfaces. During the past year, we utilized gridded ozone mixing ratios from the UARS MLS instrument to initialize contour fields, and winds from ECMWF analyses to reconstruct their time evolutions using advection on isentropic surfaces. Similar calculations were performed using potential vorticity (also from ECMWF analyses) as the initializing field. Some preliminary calculations have been carried out with encouraging results. The resulting 'reconstructed' tracer fields show features which are smaller in scale than those present in the initial field. These results have been presented at the May 1996 meeting of the European Geophysical Society in The Hague.

We have analyzed the relative dispersion properties of the flow in the lower stratosphere are analyzed in the light of theories on two-dimensional turbulence. It was determined that the flow within the polar vortex can be considered as quasi-two-dimensional, isotropic, homogeneous and stationary for periods of up to two weeks. It is found that the mean square separation between balloons released two hours apart inside the vortex (70S, 50 mb) increases in time following approximately a) the Kraichnan-Lin exponential law for small time scales (1.5 to 4 days), b) the Richardson-Obukhov t-cube law for intermediate time scales (7 to 18 days), c) an asymptotic linear behavior for large times (20 to 40 days).

We have found that individual trajectories can be quite sensitive to the method of computation. For example, trajectories calculated by using simulated velocity fields which were updated at a lower frequency in time (24 hours) show significant differences from those calculated on-line (velocity fields updated every 20 minutes). The STRATEOLE balloons, therefore, may give insight into the appropriate method for computing trajectories in the stratosphere.

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Tracer Transport in GFDL SKYHI Model

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Research Objectives

The goal of the research was to provide a theoretical basis for interpreting the large crop of new constituents data by developing a new diagnostic formalism for the Lagrangian mean motion of the stratospheric tracers. For this "tool development," we have relied on the high-resolution troposphere-stratosphere-mesosphere "SKYHI" general circulation model (GCM) run at NOAA's Geophysical Fluid Dynamics Laboratory for which "perfect observation" is possible.

Summary of Progress and Results

An increasingly pervasive view of the stratospheric transport is that the stratosphere consists of "containment vessels" of air that are dynamically separated by transport barriers, at least during certain period of the year. For example, the Antarctic air in the early spring seems well isolated by the remnant of the polar night jet, allowing the low-temperature catalytic photochemistry inside it to destroy ozone with little dilution [McIntyre, 1989; Schoeberl *et al.*, 1992; Bowman, 1993]. Plumb [1996] also proposes a similar dynamical isolation of the tropical stratosphere.

Although the containment vessel idea is simple to understand, it is not easy to formulate it in a quantitative fashion. The primary difficulty is that the container can be defined only in a Lagrangian sense and is not amenable to the traditional Eulerian transport models. Although most extant Lagrangian diagnoses depend on the particle or contour advection methods, they require solution of an initial value problem to address the transport properties and do not provide an instantaneous diagnosis of transport.

To make progress, we measured the mass enclosed by the contours of a tracer within isentropic layer. Then the tracer contour was plotted against this layer mass (area) as a horizontal coordinate. Tracer transport in this coordinate solely reflects nonconservative processes such as diffusion and diabatic effects. We derived an exact transport equation in this coordinate. In particular, a new parameter for irreversible mixing, "equivalent length," was introduced as a physically defensible alternative for the eddy diffusivity concept.

When this diagnostic was applied to the SKYHI data, the edge of the polar vortex with irregular shape was resolved much more precisely than the conventional zonal mean models. Also, the seasonal evolution of barriers was clearly identified by the isolated minima in equivalent length. The method is now being utilized for the diagnosis of UARS trace constituents data.

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Analysis of Spatial and Temporal Variability of Stratospheric Dynamics and Trace Constituents

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Research Objectives

This task uses fifteen years of National Center for Environmental Prediction (NCEP) Climate Prediction Center (CPC) data and NASA's GSFC Data Assimilation Office (DAO) data in conjunction with the GSFC 2-D, 3-D, and trajectory models to enhance our understanding of the dynamics, chemistry, and radiative properties of the middle atmosphere. In addition, Total Ozone Mapping Spectrometer (TOMS) data are routinely to assess ozone trends and variability. This task uses the currently available fifteen years of NCEP data and DAO data in conjunction with the GSFC 2-D, 3-D, and trajectory models to enhance our understanding of the dynamics, chemistry, and radiative properties of the middle atmosphere.

Summary of Progress and Results

Winds derived from the Stratospheric and Tropospheric Data Assimilation System (STRATAN) were compared with balance winds derived from NCEP heights [Coy *et al.*, 1994]. At middle latitudes in the lower stratosphere, the results showed that STRATAN winds were comparable to the balance winds and provided useful horizontal divergence analyses, and hence, vertical velocity fields. This was particularly useful for vertical transport in the CTM. Further, STRATAN wind were very useful in the tropics and the upper stratosphere where the balanced winds fail, capturing the QBO, but failing to adequately represent tropical waves.

Winds, temperatures, residual circulations, as well as case studies of polar vortex dynamics were compared for two data assimilation systems (from GSFC and UKMO) and reported in [Coy *et al.*, 1996]. It was shown that the two systems give a broadly consistent picture of the atmospheric

circulation. Where differences were identified, they could often be attributed to particular shortcomings in one of the assimilation systems. The results stressed the usefulness of data assimilation for stratospheric transport and budget studies.

We have used NCEP analyses of the polar vortex to compare ozone measurements from the MLS on UARS with soundings from a lidar system operated at mid-latitudes by the University of L'Aquila, Italy [Raedaelli *et al.*, 1994]. Lidar observations taken within the vortex showed good agreement with the UARS data.

In addition to the mid-latitude lidar comparisons, a 10% reduction of ozone was measured above the Observatoire de Haute Provence (OHP) in Southern France (43.9°N, 5.7°E) during July and August 1992 using the STROZ-LITE [McGee *et al.*, 1994]. This ozone change was correlated with the presence of volcanic aerosols from the eruption of Mt. Pinatubo.

Trajectory mapping builds synoptic maps from asynoptically gathered data by advecting measurements backward or forward in time using NCEP analyzed wind fields. This procedure was successfully applied to an analysis of dynamical wave-breaking events and an examination of Upper Atmosphere Research Satellite data accuracy [Morris *et al.*, 1995].

We developed objective criteria for choosing the location of the NH polar vortex boundary region and the onset and breakup dates of the vortex. By determining the distribution of pv on equivalent latitudes, we defined the vortex edge as the location of maximum gradient of pv constrained by the location of the maximum wind jet calculated along pv isolines. We defined the vortex boundary region to be at the local maximum convex and concave curvature in the pv distribution surrounding the edge. We determined that the onset and breakup dates of the vortex on the 450 K isentropic surface occur when the maximum wind speed calculated along pv isolines rises above and falls below approximately 15.2 m/s. We used 1992 through 1993 as a test case to study the onset and breakup periods, and found that the increase of polar vortex pv values is associated with the dominance of the term in the pv equation involving the movement of air through the surface due to the diabatic circulation. We also found that the decrease is associated with the dominance of the term involving radiatively induced changes in the stability of the atmosphere [Nash *et al.*, 1996].

Simultaneous, multiple-level contour advection and reverse domain-filling simulations of the polar vortex were performed to examine the 3-D structure of filaments [Schoeberl *et al.*, 1995]. Results showed that filaments forming at the edge have a fairly coherent vertical structure often over the whole stratosphere. The changes in Liapunov coefficient roughly correlated with the changes in the geopotential height variance, and the eddy diffusion coefficient K_{yy} for the three winters [Schoeberl *et al.*, 95].

A series of isentropic trajectory calculations were performed for emissions by stratospheric aircraft moving across the northern mid-latitude oceanic flight corridors. It was found that few parcels emitted along these flight paths at this time of year were found to have experienced nitric acid trihydrate (NAT) formation temperatures, except for the particularly cold Januarys of 1986, 1987, and 1992. These emissions are critical to the uncertainty of environmental impact assessments based on two-dimensional transport models [Sparling *et al.*, 95].

The GSFC radiation model and NCEP temperatures were used to compute polar vortex daily net heating rates in the Arctic late fall and winter and for the Antarctic fall and winter. In the NH vortex, 18 km air parcels descended 6 km between 1 November and 21 March, 25 km air

descended 9 km, and 50 km air descended 27 km. In the Southern Hemisphere (SH) vortex, 18 km air parcels descended 3 km from 21 March to 30 October, while air at 25 km descended 5-7 km. Computed descent rates increased markedly with height. The computed descent rates agreed well with observations of long-lived tracers, validating the radiative transfer model [Rosenfield *et al.*, 94].

Analysis of the NCEP data for the two SSBUV flights (March 1992 and early April 1993), indicated that the conditions in the stratosphere were very similar for these two periods [Hilsenrath *et al.*, 1996]. The temperatures had significantly warmed from winter throughout most of the stratosphere and the circulation was approaching normal summertime conditions for both periods. The SSBUV comparison for the two years showed that in the latitude range 30°N-60°N total ozone was 12% lower in 1993 than in 1992. This change was larger than the observational errors and the expected interannual variations [Hilsenrath *et al.*, 1996].

Northern mid-latitude aircraft flights in the spring of 1993 showed laminae containing high ozone concentrations, traceable to the April 1993 polar vortex break-up. These laminae were clearly traceable as polar vortex breakup fragments using pv and isentropic trajectory calculations derived from STRATAN, NCEP, and UKMO analyses. Laminae in stratospheric ozone profiles are commonly observed in the NH during fall, winter, and spring, and are hypothesized to originate from very low frequency transverse waves, or via Rossby wave breaking. Based on these results, the ozone laminae observed during Stratospheric Photochemistry Aerosols and Dynamics Expedition (SPADE) were a result of Rossby wave breaking during the breakdown of the polar vortex. Thus, conventional once per-day meteorological analyses are adequate for representing the transport of this material into the lower stratosphere mid-latitudes over the course of the spring vortex breakup [Newman *et al.*, 1996].

The damping of temperature waves by radiative processes in the stratosphere is typically represented as a linear damping directly proportional to the temperature perturbation. We calculated Newtonian cooling using the Goddard radiative transfer model and seventeen years of the NCEP analyses. Diabatic heating was found to be a strong linear function of the temperature over most of the stratosphere. Damping times of stratospheric temperatures have been calculated for each month. These calculated damping times were generally consistent with previous estimates over most of the stratosphere, but show much shorter damping time scales in the tropics [Newman and Rosenfield, 1996].

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Convectively Generated Gravity Waves

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Research Objectives

The goal of this project is to understand and quantify the importance of mesoscale convectively generated gravity waves to the tropical stratospheric momentum budget. Included in this is an examination of the nature of the gravity waves generated by convection, as revealed by aircraft measurements.

This study is motivated by clear observational evidence from aircraft and radars of significant amplitude gravity waves above tropical convective systems the fact that planetary scale waves alone cannot account for either the stratopause semiannual zonal wind oscillation or the lower stratosphere quasi-biennial zonal wind oscillation.

Summary of Progress and Results

First, we have extended the calculations of upward momentum flux as a function of wave phase speed from the September calculation done in Pfister *et al. [Journal of the Atmospheric Science*, 1993] to the full seasonal cycle. In this paper, convection was assumed to be an ensemble of transient moving convective "mountains" of constant time and spatial scale, globally distributed according to known cloudiness statistics.

As part of the effort to look at the full seasonal cycle we also examined the importance of the correlation between tropopause wind speed with the incidence of convective clouds. This is important because the nature of the distribution of upward momentum flux in phase speed depends on the relative motion of the convective system and the wind at the tropopause (where the convective system impinges on the stratosphere).

Two conclusions can be drawn from this work. First, the seasonal variation is not large. Second, the easterly bias (stronger negative momentum flux than positive) in Fig. 1a, due to the easterly movement of about 5 ms^{-1} of the idealized transient moving convective "mountains", disappears in the full calculation, because active convection in the tropics is generally correlated with strong easterly winds.

Aircraft data analysis work involves using the satellite and aircraft meteorological data to look for gravity waves generated by storm systems in the southern ocean. These gravity waves, which probably break in the mesosphere, contribute to the overall downward circulation within the Antarctic vortex. They are presently very poorly characterized, and the aircraft dataset represents

one of the first good opportunities to examine them. We have examined one case of wavelike disturbances above a cloud system and shown: (1) the disturbances are clearly gravity waves; and (2) vertical momentum flux vectors point upward and away from the cloud system, consistent with the cloud system as a source of gravity waves. These results were presented at the Southern Hemisphere Meteorology Meeting in Melbourne in late September 1994.

More recently, we have analyzed aircraft data for gravity waves generated by tropical convective systems, since recent theoretical and modeling work suggests that the simple "transient mountain at the tropopause" conceptual model can explain only part of the mesoscale gravity wave variance. One case shows that most of the momentum flux appears to be at horizontal wavelengths of about 50 km, and vertical wavelengths of about 5 to 10 km. We have also found evidence of inertia-gravity waves with horizontal wavelengths of 1000 km, consistent with studies which inferred horizontal wavelengths using vertical profiles and inertia-gravity wave dispersion relationships.

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Chaotic Advection and Inertial Gravity Wave Transport in the Middle Atmosphere

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Research Objectives

The objective of this investigation is to examine the effects of transport by large-scale isentropic motion and higher frequency small-scale velocity fluctuations on the distribution of trace species in the lower stratosphere. Lagrangian analysis techniques, stratospheric datasets, global meteorological analysis, and specialized sub-models are used to investigate exchange processes in and near the stratospheric polar vortices [Pierce *et al.*, 1994 a, b]. In addition to this base theory task, Dr. Pierce, Dr. Grose, and Mr. Fairlie served as Theory Team members in the 1994 Airborne Southern Hemisphere Ozone Experiment (ASHOE). The Lagrangian analysis package developed under this proposal was used during the ASHOE campaign to characterize the morphology of the Antarctic vortex and to predict the occurrence of vortex filamentation for pre-flight planning. In addition, predictions of the evolution of airmasses observed by HALOE were conducted to determine the distribution of O_3, H_2O, and CH_4 in the lower stratosphere. A new objective for this research task has been to examine the feasibility of using HALOE airmass/photochemical box model predictions to characterize the photochemistry of airmasses observed by HALOE. Photochemical predictions have been compared with coincident *in situ* measurements of stratospheric trace gases made by instruments onboard the ER-2 during ASHOE [Pierce *et al*, 1996a]. These predictions were then used to examine chlorine deactivation during the final ASHOE deployment [Grooss *et al.*, 1996]. This photochemical modeling effort has been in collaboration with scientists from the Max Planck Institute for Chemistry in Mainz, Germany.

Summary of Progress and Results

- Exchange processes in the Northern and Southern Hemisphere (NH and SH) polar vortices during 1992 were examined [Pierce *et al.*, 1994a]. A moderate to strong kinematic barrier to large-scale isentropic exchange was identified during both of these periods. Mixing timescales within the polar night jet were found to be greater than 20 days. Differential diabatic descent

was found to have a significant impact on the mixing processes in the SH middle stratospheric jet core. The impact of small-scale displacements by idealized inertial gravity waves on the mixing times scales was also investigated and were found to have a significant impact in the vicinity of the polar night jet in both hemispheres.

- The distribution of dehydrated air in the middle and lower stratosphere observed by the Halogen Occultation Experiment (HALOE) during the 1992 SH spring was investigated [Pierce et al., 1994b]. Analysis of HALOE $2CH_4 + H_2O$ data showed that descent in the interior of the polar vortex and lateral mixing of interior dehydrated air with normal jet core air produces a radial gradient within the lower-stratospheric polar vortex while vortex filamentation causes irreversible transport of jet core air into SH middle latitudes.
- HALOE airmass/photochemical box model predictions of the evolution of airmasses observed by HALOE during SH winter and spring of 1994 were conducted and compared to coincident *in situ* observations by instruments onboard the ER-2 [Pierce *et al.*, 1996a]. The study indicates that the HALOE airmass/box model calculations were successful in predicting the distribution of HO_2, ClO, O_3, NO_y and NO observed by the ER-2. A companion study [Grooss *et al.*, 1996] investigated the partitioning of chlorine species in the lower stratosphere in late Antarctic spring using the HALOE airmass/box model. This study successfully simulated the fast conversion of active chlorine species into HCl during the Southern Hemisphere late spring.
- The ability of Lagrangian Reverse Domain Filling (RDF) predictions of the global potential vorticity (PV) distribution to capture the observed variability of long lived tracers sampled by the ER-2 during ASHOE was quantified (Fairlie *et al.*, 1996). The results of this analysis indicate that RDF PV shows no statistically significant improvement in forecast skill over Analyzed PV.
- *In situ* wind and temperature observations during both 1994 (ASHOE) and 1987 (AAOE) aircraft campaigns have been used to relate small scale wind (SSW) direction and magnitude to the large-scale flow for the SH lower stratosphere.
- This analysis was used to develop a parameterization of the statistical effects of observed SSW for incorporation into the Lagrangian analysis package [Pierce, 1995]. RMS meridional displacements associated with SSW ranged from 1 degree near the polar kinematic barrier to 8 degrees in middle latitudes during vortex filamentation events. Mean meridional displacements were generally less than 1 degree and restricted to middle latitudes.
- HALOE observations of stratospheric H_2O and CH_4 were used to examine the seasonal evolution of water vapor on methane surfaces. This analysis provides a clear picture of the seasonal transport of dry air into middle latitudes from its source regions in the tropics, the Antarctic polar vortex, and the lower mesosphere. A manuscript [Pierce *et al.*, 1996b] has been prepared describing this research but small systematic errors in the HALOE V17 water vapor retrieval has dictated waiting for the V18 retrieval to be completed before submission.

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Studies of Interannual Stratospheric Variability Related to Global Change

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Research Objectives

The objective of this work involves the analysis of long time records of stratospheric dynamical and constituent data obtained from satellite measurements, with the aim of quantifying sources of interannual variability in the stratosphere. These studies are based on data spanning 1978 to present, including TOMS and SBUV-SBUV/2 ozone, SAGE II ozone and nitrogen dioxide, and MLS + HALOE observations from UARS, combined with TOVS stratospheric temperature data and meteorological analyses from NCEP. The main goal is to quantify correlated interannual variations in dynamical and constituent data, using a variety of space-time statistical analyses.

Summary of Progress and Results

We have performed a variety of analyses related to satellite ozone observations. We have combined the SBUV and SBUV/2 datasets into a continuous daily global record spanning 1978 through 1994, and published a detailed climatology (including variability statistics). TOMS ozone data have been analyzed in conjunction with meteorological data to document correlated variability; one important result is evidence of cooling in the lower stratosphere associated with the recent ozone depletions. The global signatures of Mt. Pinatubo on stratospheric ozone and temperature were also quantified. Space-time structures of the quasi-biennial oscillation (QBO) in ozone and nitrogen dioxide have also been isolated, with focus on mechanisms for the mid-latitude lobe of the QBO. UARS tracer observations have been analyzed in conjunction with general circulation model results to quantify stratospheric transport budgets and their interannual variability.

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Dynamical Coupling of the Troposphere and Stratosphere

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Research Objectives

The dynamical coupling of the troposphere and stratosphere is studied using a global, nonlinear, primitive equations model. A principal goal is to find out how the transient planetary wave events that disturb the stratosphere are generated in the troposphere, and to determine whether this process is sensitive to the state of the stratosphere or whether it is governed primarily by tropospheric events. Related objectives are to investigate the downward influence of stratospheric events on the troposphere, and to look for evidence of stratospheric multiple equilibria.

Summary of Progress and Results

Extended runs of a global, spectral, primitive equations model, adapted from that developed by Dr. Richard Young and his collaborators at the NASA Ames Research Center, have been performed. Substantial low-frequency variability is found in stratospheric wave activity even in a perpetual winter model with no stationary wave forcing. The stratospheric mean flow acts as a very effective filter for tropospheric wave forcing - only planetary waves 1 and 2 with periods in excess of 40 days are found in the stratosphere.

The nonlinear source of these planetary wave events is being analyzed using a linear version of the model, driven by different nonlinear terms saved from the full simulation. It appears that both heat and vorticity fluxes by synoptic waves are important, as is the tropospheric baroclinicity of the nonlinearly forced planetary waves.

Publications

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Dynamical and Chemical Behavior of the Lower Stratosphere and Interactions with the Troposphere

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Research Objectives

This research program focuses on planetary waves, synoptic disturbances, and organized convection and how, through vertical and horizontal transport, these components of the tropospheric circulation influence the chemical composition and energetics of the stratosphere. Because these processes shape stratospheric behavior, this research throws light on how ozone is coupled to tropospheric behavior and, consequently, on how it may evolve through long-term changes in tropospheric forcing.

Summary of Progress and Results

Equivalent-barotropic calculations, in tandem with Lagrangian analyses, reveal how diabatic motions comprising the Brewer-Dobson circulation develop from quasi-horizontal advection by planetary waves. Potential temperature along a material surface indicates organized subsidence inside the polar-night vortex, resembling tracer observations. Lagrangian histories illustrate that this sinking motion follows from parcels being driven out of thermodynamic equilibrium by planetary waves. Irreversible heat transfer then produces a net drift of air across isentropic surfaces as parcels orbit about the displaced vortex. By driving mean-meridional overturning in the stratosphere, this downward drift is ultimately responsible for transferring ozone from the tropics to the extratropical lower stratosphere. It also introduces horizontal structure into the distribution of total ozone, which surfaces clearly in ozone trends.

High-resolution global cloud imagery constructed from 6 satellites simultaneously observing the Earth was used to investigate the spectrum of equatorial waves generated by tropical convection and propagating vertically into the stratosphere. The results indicate that temperature variability is dominated by planetary-scale equatorial waves like the Kelvin mode, which agrees with satellite observations of the tropical stratosphere. However, the Kelvin mode accounts for only about 30 to 50% of the eastward momentum flux radiating into the stratosphere, the remainder coming from gravity waves.

An algorithm was developed to determine 3-D atmospheric motion from satellite tracer measurements. Based on Lagrangian constraints, the algorithm circumvents limitations of the traditional scheme for inferring motion from temperature measurements and determines the circulation in the tropics as reliably as elsewhere. Intraseasonal variations in the tropics, which modulate tropopause height and convective transport there, was investigated in calculations of how planetary waves interact with organized convection. Those calculations reproduce observed

features of the so-called Intraseasonal Oscillation and show that the accompanying Kelvin structure can propagate well into the stratosphere.

A study of deep convection revealed that the highest towers (those penetrating into stratospheric air and controlling tropopause height and composition through convective mixing) occur in close association with the diurnal cycle of convection.

Clouds colder than 220~K develop almost entirely in association with the diurnal cycle of convection over tropical landmasses and substantially in association with it even over maritime regions. Towards understanding the mean structure and seasonality of total ozone, we developed a 3-dimensional model of stratospheric transport and photochemistry, based on the primitive equations in isentropic coordinates. Fully spectral, this mechanistic model is forced by observed tropospheric behavior on an isentropic surface and treats 36 chemical species. It has been used along with Lagrangian analyses to study how 3-D transport and photochemical production lead to observed structure in the distribution of total ozone. These calculations reveal directly how nonconservative effects associated with dynamics and photochemistry combine to produce observed variations in total ozone and how those features may evolve in response to long-term changes in tropospheric forcing. The results should be useful for interpreting mid-latitude ozone changes.

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B. Atmospheric Chemistry Analysis and Related Modeling

Analysis of ATMOS Water Vapor Data

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Research Objectives

This research task deals with an analysis of the water vapor data of the upper troposphere and stratosphere retrieved from observations by the Atmospheric Trace Molecule Spectroscopy (ATMOS) Experiment from four space shuttle missions carried out from May 1985 to October 1994. The vertical profiles of H_2O, CH_4, and a number of chemically related species have been obtained from analysis of the observed data over a wide range of latitudes and geographical locations. The objectives of this research are to examine the ATMOS data for evaluations of hydrogen budget of the stratosphere and investigate the sources and variability of water vapor in the stratosphere.

Summary of Progress and Results

The stratospheric water vapor is determined by a combination of chemical and dynamical processes. Chemical processes involving the oxidation of CH_4 enhance the abundance of H_2O, producing approximately two molecules of H_2O for each molecule of CH_4 and leading to higher H_2O mixing ratios with altitude relative to air entering the stratosphere. A portion of the H_2O and CH_4 data retrieved from observations during the four ATMOS missions for the northern mid-latitudes and tropics has been analyzed for evaluations of $H = (H_2O + 2CH_4)$, the annual average H_2O mixing ratio transported to the stratosphere, for evidence of seasonal variation of water vapor entering into the stratosphere, and for estimates of the distribution of molecular hydrogen in the upper stratosphere and the lower mesosphere.

The measurements indicate an average value of 7.24 ± 0.44 ppmv for H between altitudes of about 18 to 35 km, corresponding to an annual average water vapor mixing ratio of 3.85 ± 0.29 ppmv entering the stratosphere. The H_2O vertical distribution in the tropics exhibits a wave-like structure in the 16 to 25 km altitude range suggestive of seasonal variations in the water vapor transported from the troposphere to the stratosphere. The hygropause appears to be nearly coincident with the tropopause at the time of observations. This is consistent with the phase of the seasonal cycle of H_2O in the lower stratosphere, since the ATMOS observations were made in November when the H_2O content of air injected into the stratosphere from the troposphere is decreasing from its seasonal peak in July/August.

An examination of measurements of H_2O and CH_4 made by ATMOS indicates that the quantity $H = (H_2O + 2CH_4)$ is conserved in the lower and middle stratosphere and yields an average water vapor entry into the stratosphere of 3.70 ± 0.28 ppmv. H is not conserved in the upper stratosphere and lower mesosphere; it reaches a maximum at ~50 to 55 km, then decreases with height. This structure is evident in the correlation plots of H_2O vs. CH_4 for all four missions. The region near ~50 km is characterized by an excess abundance of H_2O ~ 0.4 ppmv, providing evidence of a source of H_2O from oxidation of H_2, whereas the decrease in H observed at higher altitudes implies net production of H_2 from H_2O and CH_4. The distribution of H_2 inferred from variation of H with altitude indicates a sickle-shaped profile with a constant mixing ratio at altitudes of $\leq$ 35 km, a minimum at ~50 km, and increasing to > 1 ppmv above 65 km. The inferred distribution of H_2 is in qualitative agreement with the values obtained from a 2-dimensional coupled photochemical-dynamical model.

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Improved Determination of Atmospheric Ozone by Combining Data from IR and UV Sensors on NOAA Satellites

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Research Objectives

The first phase of this research is to assess the feasibility of producing an improved ozone product by combining data from the 9.7 μm channel 9 of TOVS on NOAA's operational Polar Orbiting Environmental Satellites (POES) and SBUV/2 which flies on the afternoon POES satellites. TOVS channel 9 is sensitive to the ozone profile primarily in the lower stratosphere as well as to the atmospheric temperature profile, lower tropospheric water vapor, and surface skin temperature and emissivity. SBUV/2 is sensitive to the total column abundance of ozone and has very little sensitivity to atmospheric temperature and water vapor. Surface and cloud effects are accurately accounted for in the SBUV/2 ozone retrieval algorithm. SBUV/2 is capable of resolving the vertical structure of the ozone profile in the upper stratosphere, but is unable to resolve the fine structure in the lower stratosphere and troposphere. The cross-track scanning TOVS instrument provides nearly global coverage daily while the nadir-viewing SBUV provides only a small number of samples per day. The ultimate goal of this research is to develop a total ozone retrieval algorithm capable of utilizing the assets of both TOVS and SBUV/2 and perhaps to improve upon the SBUV/2 ozone profile retrieval. However, before this can be done, we must carefully examine whether TOVS radiances can be computed accurately enough to obtain a reasonable product. Therefore, the initial phase of this research involves the use of co-located SBUV-derived ozone profiles and TOVS Pathfinder retrievals and cloud-cleared radiances to determine whether there are significant systematic errors in the TOVS measurements or radiative transfer calculations and if so whether these errors can be corrected to an acceptable level.

Summary of Progress and Results

Our initial studies have been performed on four separate data periods for the NOAA 11 satellite; March, 1989, September 1989, October 1989, and March 1990. Two radiative transfer algorithms were used to compute TOVS channel 9 brightness temperatures: (1) the algorithm used in the TOVS Pathfinder Path A product generation provided by J. Susskind and M. Sienkiewicz (henceforth referred to as the Susskind algorithm); and (2) an algorithm similar to the one being developed for the AIRS instrument provided by Larrabee Strow. The input to the radiative transfer calculation consists of: (1) Pathfinder Path A retrievals of temperature and water vapor profiles, and surface skin temperature; (2) collocated SBUV/2 retrievals of the ozone profile in 12 layers; and (3) specified surface emissivity of 0.98 over ocean and 0.95 over land. The computed brightness temperatures are compared with Pathfinder Path A observed clear or cloud-cleared channel 9 brightness temperatures.

The comparison revealed systematic differences between observed and computed brightness temperatures. In an effort to correct these biases, we first examined the sensitivity of the channel 9 brightness temperature to changes in optical depth of water vapor and ozone separately using clear ocean scenes only. Susskind's model was found to require ~40% reduction in water vapor absorption. The ozone absorption did not require any adjustment. Strow's model required a 10 to 20% enhancement in water vapor absorption. Strow's model also required no adjustment to the ozone absorption.

Several geographically dependent biases remained after the above adjustments to the radiative transfer algorithms were applied. For example brightness temperatures computed over dessert areas, particularly the Sahara and Australia, were significantly higher than the observations. This difference can be explained by the use of an incorrect emissivity. Over quartz sand areas, the 9.7 μm emissivity is lower than that of the 11.1 μm HIRS2 channel 8 that is used to compute the surface skin temperature, but in the radiative transfer models, the emissivity is assumed to be constant over this wavelength region. We can use the co-located SBUV ozone profile and corrections to the radiative transfer algorithm derived above to estimate a correction to the 9.7 μm emissivity over these regions.

Several unexplained differences between the observed and computed channel 9 brightness temperatures still remain over ocean areas. Positive biases using both radiative transfer models (1-3 degrees) are seen over the south Pacific in September 1989. Negative biases in both models (~2 degrees) are seen over the ocean below Africa in October 1989. A sensitivity analysis determined that these differences were too large to be explained by the expected error in the SBUV-retrieved profile. A likely candidate for producing such biases is the error in the fast model parameterization. We note that in some of the areas with large biases, the biases using the Strow model are significantly less (~1K) that those using the Susskind model. It will be relatively easy to check whether the fast model is indeed producing such biases by doing line-by-line calculations and comparing against the fast model calculations for the areas in question. If the biases cannot be explained by the radiative transfer algorithm, we will try to determine whether errors in the TOVS Pathfinder data used for the radiative transfer calculations are responsible for the biases. However, this will be difficult as there is a lack of conventional data (e.g., radiosondes) in the problem areas.

It is not clear at this time whether it is worthwhile to proceed to the next phase of this project. That decision will be made when the current data analysis is complete and the development of a comprehensive bias correction model is in place. When the current analysis is complete, a manuscript will be prepared for journal publication.

Publications

None

Determination of Surface Ultraviolet Flux Using Satellite Data

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Research Objectives

A method has been developed to estimate the surface ultraviolet flux from the measurements made by the Total Ozone Mapping Spectrometers (TOMS) on NASA satellites. It is an objective of this proposal to use an accurate radiative transfer program to estimate the attenuation of incoming solar radiation above the atmosphere (provided by two instruments on NASA's Upper Atmospheric Research Satellite) by the stratospheric and tropospheric ozone column, surface reflectivity, clouds, and aerosols (the latter 4 are derived from TOMS data). A major portion of the proposal's objectives are contained in deriving an improved cloud property algorithm, a method of estimating surface reflectivity effects, and a detailed analysis of the occurrence of aerosols and their effects on UV radiation. The derived UV data are to be validated with well calibrated ground-based measurements. Finally, a database of surface UV from 1979 to the present (where there are TOMS data) is to be produced on CD-ROM and distributed by the Goddard DAAC.

Summary of Progress and Results

As part of the proposed work, a database of surface UV fluxes has been derived that include cloud effects, terrain height, surface reflectivity, ozone absorption, and aerosol effects. The effect of surface reflection is estimated by using a newly derived global monthly database of surface reflectivity at 380 nm constructed from 14.5 years of TOMS measurements (to be published by Herman and Celarier). Comparison with ground-based measurements indicate that the satellite estimates are at least as good as a well-calibrated ground-based instrument for estimating average weekly UV flux at any location on the Earth. The advantage of the satellite technique is its global coverage, extremely high relative accuracy (for studying spatial, temporal and spectral variability), and 16+ years of data record.

Eck *et al.* [1995] showed that TOMS data could be used to make highly accurate estimates of surface UV flux in both clear and cloudy conditions. They estimated the clear-sky flux using an accurate radiative transfer program that accounted for the attenuation of incoming solar radiation by the atmospheric ozone. Based on the analysis of TOMS reflectivity data they noted that the effect of surface reflectivity on the UV flux is small for snow/ice-free surfaces. UV-flux attenuation by clouds and aerosols was estimated using a simplified model that assumed them to be a translucent Lambertian-surface. Results from this simplified model compared surprisingly well with ground-

based measurements of surface UV made by a well calibrated Brewer station near Toronto, Canada. This technique was used to generate a CD-ROM containing daily values of erythema-weighted surface UV over the entire globe for the period 1978-1993 using 14.5 years of TOMS data collected from the Nimbus 7 satellite. Using this dataset Herman *et al.* [1996] estimated the long-term trend in surface UV as a function of latitude. They noted that between 1978 and 1993 TOMS data showed no statistical change in cloud/aerosol albedo. Therefore the long-term UV-trend (moderate UV increases) is determined solely by the well-recorded depletion in atmospheric ozone. This result disagrees with the strong UV decreases derived from an earlier ground-based set of measurements made by the US Robertson-Berger meters and are believed to be due to calibration problems with these instruments.

Detailed comparison with ground-based instruments have shown that the satellite technique could be improved by replacing the simple Lambertian model of cloud and aerosols with a model based on Mie scattering theory. In addition, a monthly global database of surface reflectivity constructed from 14.5 years of TOMS 380 nm radiances has been created to better account for the effects of snow/ice on the surface UV flux. The software that implements the new algorithm is now complete. In the next few months a 16-year global dataset of daily surface UV flux will be released on CD-ROM and the current data would be made available through the TOMS WWB site at NASA Goddard Space Flight Center.

Publications

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SUSIM Data Analysis

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Research Objectives

Solar UV spectral irradiance measurements were made by the Solar Ultraviolet Spectral Irradiance Monitor (SUSIM) experiment on the Atmospheric Laboratory for Applications and Science (ATLAS) series of space shuttle missions. These measurements and the necessary calibrations to permit conversion to high accuracy absolute spectral irradiance exist for ATLAS flights in March 1992, April 1993, and November 1994. Further reduction and analysis of the ATLAS data has produced improved results that have been published and used in papers comparing and validating space flight experiment such as the UARS SUSIM, UARS SOLSTICE, ATLAS SSBUV, and ATLAS SOLSPEC instruments. The SUSIM ATLAS data is being widely used as a high-resolution standard extra-terrestrial solar ultraviolet spectra by ground-based investigators.

Summary of Progress and Results

Further reduction and analysis of the SUSIM ATLAS 3 pre- and post-flight calibration data has led to a greater understanding of the correction coefficients to be used for the 0.15 nm high-resolution solar ultraviolet irradiance spectra. Two significant improvements have been made. The first is an improvement in determining the wavelength scale for the high resolution data which has reduced the 2 wavelength uncertainty to 0.035 nm. The second is an improvement in the determination of the absolute irradiance calibration coefficients and the aging corrections which led to a 3% 2 irradiance uncertainty for the 150- to 410-nm high-resolution spectra. This is a significant improvement over the earlier SUSIM SPACELAB-2 spectra which was used for the ultraviolet section of World Data Center solar spectral irradiance standard. The improvement in the wavelength accuracy is important to models of the upper atmosphere as well as investigators of ground level UV-A and UV-B levels. An accurate modeling of the solar spectraís interaction with the complex atmospheric absorption is important to many models of the atmospheric. The rapid change in ultraviolet flux in the UV-A and UV-B regions requires high accuracy in the ground measurements and extra-terrestrial solar spectra in order to establish proper indexes.

These improvements in calibration of the ATLAS 3 flight and have been applied to the 13 November 1994 solar viewing period to produce a high-resolution solar spectra which is being published and has been placed on the SUSIM web site for access by the scientific community. This spectra has also been used for comparisons with data from the SUSIM UARS and ATLAS 3 SSBUV instruments. SUSIM ATLAS results have also been used in detailed comparison and validation projects with SUSIM UARS, UARS SOLSTICE, ATLAS SSBUV, and ATLAS SOLSPEC instruments. These inter-comparison efforts give added confidence to the accuracy now being obtained in the measurements of the absolute solar ultraviolet irradiance. Each of the instrument groups has been able to refine their reduction and analysis techniques to eliminate problems which were uncovered through these inter-comparison activities. Publication of these comparisons assist solar ultraviolet spectral irradiance data users and future investigators.

Publications

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Analysis of Solar Spectral Irradiance Measurements from the SBUV/2-Series and the SSBUV Instruments

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Research Objectives

Short-term and long-term variations in solar ultraviolet (UV) spectral irradiance play a significant role in stratospheric ozone variations. Recent work indicates a 1.5 to 2% solar cycle variation of global mean total ozone as well as solar cycle-driven variations in lower stratospheric temperature and geopotential height. The Solar Backscatter Ultraviolet, Model 2 (SBUV/2) instruments perform daily UV solar irradiance measurements, however do not include onboard calibration systems necessary to maintain the instruments' calibrations for long-term solar monitoring. The primary goal of this research activity is to use simultaneous data obtained from October 1989 through November 1994 with the Shuttle SBUV instrument (SSBUV) to correct for long-term drift in the NOAA 11 SBUV/2 instrument, and thus create a calibrated NOAA 11 SBUV/2 middle UV solar irradiance dataset for that period which is available for additional research. Comparisons of the SBUV/2 and SSBUV solar measurements with corresponding data from the Upper Atmosphere Research Satellite (UARS) Solar Stellar Irradiance Comparison Experiment (SOLSTICE) and Solar Ultraviolet Solar Spectral Irradiance Monitor (SUSIM) instruments, as well as the Space Shuttle-based Atmospheric Laboratory for Applications and Science (ATLAS) SUSIM and Solar Spectrum (SOLSPEC) instruments data are also being performed. Finally, an improved SBUV/2 Mg II solar activity proxy index is being developed and analyzed.

Summary of Progress and Results

1994: This research commenced in September 1994. The initial effort focused on development of UNIX-based software tools necessary to process the SBUV/2 and SSBUV solar irradiance data and perform the research. Previously, preliminary research and data processing were performed on a NASA GSFC IBM mainframe computer. As this computer was scheduled for removal during 1995, roughly 1800 MB of data and software were transferred to a UNIX workstation.

Comparisons of the NOAA 9 and NOAA 11 "day 1" solar irradiances with the SSBUV solar data began during this time period. Initial comparisons of the preliminary SSBUV solar irradiance data

from the ATLAS 1 and ATLAS 2 missions with the corresponding UARS and other ATLAS instruments' solar data began. A seventh SSBUV mission was flown in November 1994. Near real-time comparisons of the three ATLAS solar spectral irradiance instruments' data were performed.

1995: Activities centered on analysis and understanding the SSBUV instrument's radiometric calibration and in-flight performance for the first six Shuttle flights. Coincident with our enhanced understanding of the SSBUV instrument's performance characteristics were similar improvements in the calibrations of the other ATLAS and UARS instruments. Detailed comparisons of the solar irradiance data obtained by the three ATLAS and two UARS UV solar irradiance instruments were performed. Analysis of lunar albedo data acquired during the ATLAS 3 mission was undertaken and completed. Three papers were submitted for publication in 1995.

Coincident with these activities, we began to update the characterizations of the NOAA 9 and NOAA 11 SBUV/2 instruments using internal data. Thorough internal calibration is necessary before comparisons with the SSBUV datasets can be used to provide the satellite instrument's long-term calibration.

The NOAA 14 SBUV/2 instrument began solar observations in early 1995. Initial comparisons of the NOAA 14 solar data with data from other instruments were performed. Beginning in April 1995 the instrument began to experience serious difficulties in its wavelength drive system and significant resources were devoted to characterizing the problems. The problems continued to worsen and NOAA 14 sweep mode solar observations were discontinued in October.

1996: The ongoing internal characterization of the NOAA 11 and NOAA 9 SBUV/2 solar datasets is nearing completion. Solar irradiances from the first seven SSBUV flights were finalized and an eighth flight occurred in January 1996. Final calibration of the NOAA 11 solar data via SSBUV is planned for late summer. Revised and extended Mg II datasets from NOAA 9 and NOAA 11 are being produced and compared to corresponding UARS SOLSTICE and SUSIM Mg II data. Detailed analysis of the SBUV/2 Mg II data is also underway. Additional comparisons of the SSBUV and SBUV/2 data with corresponding GOME data are being performed.

Dr. Cebula is Leader of the Middle UV Working Group (WG2) of the Solar Electromagnetic Radiation Study for Solar Cycle 22 (SOLERS22), a Solar Terrestrial Energy Program (STEP) sponsored international collaborative research effort. Dr. Cebula served on the Scientific Organizing Committee of the SOLERS22 1996 Workshop, held 17-21 June 1996 at Sacramento Peak Observatory, Sunspot, New Mexico. Mr. DeLand also participated in this workshop. Four papers related to this research were presented at the workshop as was the WG2 Workshop Report. Each paper will be submitted to Solar Physics for publication.

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US Participation in the GOME and SCIAMACHY Projects

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Research Objectives

The research at the SAO for the GOME and SCIAMACHY projects includes

- Development and maintenance of scientific software for the GOME retrieval algorithms,
- Advice and assistance in the development of GOME operational software,
- Participation in GOME validation studies,
- Sensitivity and instrument studies to help finalize the definition of the SCIAMACHY instrument,
- Development of the Scientific Requirements Document for Data and Algorithm Development,
- Development of scientific software for SCIAMACHY retrievals, and
- Consultation on optical and detector issues for both GOME and SCIAMACHY. GOME was successfully launched in April 1995 and is currently operating normally. A new development in this research is a series of European ozone monitoring instruments (OMI) based, to an extent that is currently under discussion, on GOME. These will fly on the Metop series of operational meteorological satellites being planned by Eumetsat. Kelly Chance is the US member of the OMI Users Advisory Group.

Summary of Progress and Results

GOME

Operational processing code for GOME total column trace gas retrieval is completed and validated. The development of the scientific code that will implement the GOME height-resolved O_3 retrieval algorithms and, eventually, their realization as operational processing code, is well underway. All GOME code will naturally evolve into SCIAMACHY code with the additional incorporation of (a) appropriate infrared line-by-line and ESFT-based band-model forward modeling capability and (b) the limb and occultation measurement geometries of SCIAMACHY. GOME studies at SAO to date include:

- Chairing the GSAG Data and Algorithm Subcommittee.
- Guiding the development of GOME Level 0-1 and 1-2 operational software through extensive collaboration with the DLR;

- Investigation of cloud studies, including fitting schemes and analysis of uncertainties due to various error sources, including line parameters of O_2. This formed the basis for the operational algorithm for GOME cloud correction, implemented in the Level 2 operational software. In addition, an improved molecular line database for the visible A band of O_2 has been developed and compiled.
- Substantial improvements to the GOMEware scientific code framework for thorough scientific testing of GOME algorithms, including those that have been implemented initially and those that are under development. This includes the implementation of the SBUV code in the GOMEware, and its testing for a variety of simulated GOME measurements, and inclusion of GOMEware structures in the GOMEtran finite-difference method forward model.
- Participation in GOME validation and scientific studies. The SAO proposal in response to the ESA Announcement of Opportunity for the ERS mission has been selected. K. Chance is now a "GOME Validation Principal Investigator." Note that the validation studies include the first ozone profiles and tropospheric ozone abundances, which (in the first operational phase) will be produced as off-line scientific products. The validation studies include extensive intercomparisons of data and algorithms with the SBUV/TOMS instruments. These are currently in progress.
- Collaboration on the development of the DOAS method as the operational procedure for GOME Level 1-2 processing to produce O_3 columns from GOME. This collaboration includes code development, measurement window selection, and a number of related issues.
- Participation in GOMEtran forward model development, in collaboration with the University of Bremen. The GOMEtran radiative transfer code has been released and is currently being used for initial height-resolved ozone retrieval studies.
- Spectroscopic and aerosol database development.
- Radiative transfer studies related to wavelength calibration, spatial and spectral aliasing, and improved Ring effect modeling.
- Collaboration in scientific studies using GOME data, including the measurement of BrO and OClO from GOME.

SCIAMACHY

- Definition of SCIAMACHY instrument, including: consultation on detector, cooling and instrumentation issues; finalization of the band definitions and detector selection criteria; synthetic retrieval studies for atmospheric spectroscopy in the infrared.
- Chairing the scientific working subgroup for Algorithm Development and Data Usage, including organization of joint GOME/SCIAMACHY science workshops and heading the development of a Scientific Requirements Document for SCIAMACHY Data and Algorithm Development.
- Radiative transfer studies, including acquisition of AVIRIS data for determination of infrared albedos for a number of measurement locations.
- Initial extension of the GOME software development to SCIAMACHY. In particular, this requires the inclusion of limb and occultation geometries, and extension into the infrared, with line-by-line and ESFT band models. Some preliminary database issues involved in this development have been addressed. The issue of properly combining limb and nadir

measurements is being addressed in conjunction with the development of the SCIAMACHY observational strategy, in the context of the Algorithm Development and Data Usage subgroup.

- Contributions to the SCIAMACHY Instrument Requirements Document.
- Contributions to the SCIAMACHY Scientific Requirements Document.

OMI

Participation in development of the User Requirements Document, addressing data analysis algorithm issues, and advising on the instrument configuration.

Publications

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Modeling of the Partitioning of Reactive Odd Nitrogen in the Lower Stratosphere Using Aircraft Measurements of NO_y, NO, and Other Species

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Research Objectives

The suite of simultaneous measurements available on the ER-2 includes a wide variety of long-lived and reactive species. The time and location of measurements includes periods in all seasons, altitudes in the upper troposphere and lower stratosphere, and a wide latitude range in both hemispheres. The goal of this task is to use these ER-2 observations and models to address the distribution and partitioning within the NO_y reservoir, the controlling photochemical and transport processes, and the interaction of the NO_y reservoir with other reactive species. Included in this effort are local steady state, trajectory, full-diurnal photochemical, and two-dimensional (2-D) models.

Summary of Progress and Results

Interpretive efforts have continued using data from the 1994 Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) aircraft campaign and the NASA Stratospheric Tracers of Atmospheric Transport (STRAT) mission.

Publications include the Concorde sampling study [Fahey *et al.*, 1995], in which emission indices of reactive gases and particles were determined from ASHOE/MAESA measurements made in the Concorde exhaust plume while the aircraft was at supersonic cruise in the stratosphere. Values for NO_x agreed well with ground-based estimates. Measurements of NO_x and HO_x indicated a limited role for HNO_3 in the plume. The large number of submicron particles measured implied efficient conversion of fuel sulfur to H_2SO_4 in the engine or at emission. A new fleet of supersonic aircraft with similar particle emissions will significantly increase stratospheric aerosol surface areas and may increase ozone loss above that expected for NO_x emissions alone.

In Keim *et al.* [1996] and Nevison *et al.* [1996], measurements of NO_y and N_2O from ASHOE/MAESA are used to examine changes in the NO_y-N_2O correlation over a broad range of latitude and season in both hemispheres. The correlation plots reveal compact, near-linear curves throughout the dataset. The correlation plots show a distinct and seasonally dependent hemispheric asymmetry, with a much larger seasonal variation in the average slope of the correlation, $\Delta NO_y/\Delta N_2O$, in the Southern Hemisphere (SH). Between March and October 1994 in the potential temperature range of 400 to 525 K, the slope of the correlation in the SH mid-latitudes increased by

30%. A smaller but still positive increase in the slope of the correlation was observed for data obtained within or near the edge of the SH polar vortex. The observed increase in the slope is consistent with ongoing descent throughout the winter and spring, and suggests that irreversible loss of HNO_3 through sedimentation of cloud particles (denitrification) is not a significant term (< 10-15%) in the wintertime NO_y budget at SH mid-latitudes. However, the observations and 2-D model results both suggest that vortex denitrification and dilution into mid-latitudes when the vortex breaks up in the spring play a significant role in the observed SH seasonal cycle for the NO_y-N_2O correlation.

In Fahey *et al.* [1996], ASHOE/MAESA measurements of NO_y and ozone made in the lower stratosphere are used to examine the NO_y/O_3 ratio over a broad latitude range (60°N to 70°S) during two different seasons (March and October 1994). Both NO_y and ozone mixing ratios show a strong latitude dependence, with values increasing toward the poles. The NO_y/O_3 ratio reveals a high-gradient region near the tropics as observed in previous datasets. Values are lowest in the inner tropics and nearly constant poleward of the gradient region, particularly in the spring. Comparisons of NO_y/O_3 values with 2-D model calculations show important discrepancies, most notably near the high-gradient region. In one model, the agreement can be improved by changing the horizontal eddy diffusion coefficients near the tropics. The simulation of the NO_y/O_3 ratio is an important diagnostic check for 2-D models used to predict the impacts of stratospheric aircraft emissions.

In Gao *et al.* [1996], ASHOE/MAESA measurements of NO, NO_2, and total reactive nitrogen (NO_y, = NO + NO_2 + NO_3 + HNO_3 + $ClONO_2$ + $2N_2O_5$ + ...) are examined. Comparisons between measured NO_2 values and those calculated using a steady-state (SS) approximation are presented for flights where NO_2 measurements are available. The SS results show good agreement with the measurements, suggesting that calculations of the NO_2 photolysis rate are accurate for the lower stratosphere. Further model comparisons using a full-diurnal photochemical steady-state (PSS) model also show good agreement with the NO and NO_2 measurements, suggesting that the partitioning of the NO_y reservoir can be well represented in the lower stratosphere.

In Volk *et al.* [1996], airborne *in situ* observations of CH_4, N_2O, NO_y, ozone, chlorinated halocarbons, and Halon-1211, used in a tropical tracer model, show that mid-latitude air is entrained into the tropical lower stratosphere within ~13.5 months; transport is faster in the reverse direction. Because exchange with the tropics is slower than multi-dimensional models generally assume, ozone at mid-latitudes appears to be more sensitive to elevated levels of industrial chlorine than currently predicted. Nevertheless, approximately 45% of air in the tropical ascent region at 21 km has been entrained from mid-latitudes, implying that emissions from supersonic aircraft could deplete ozone in the middle stratosphere.

Del Negro *et al.* [1996] examine measurements in air that was encountered in the early stages of recovery from polar stratospheric cloud (PSC) processing during the third deployment of the ASHOE/MAESA campaign. The air had unusual partitioning within NO_y and Cl_y caused by low ozone and ClO values. The NO/NO_y ratio was as high as 0.5 and the HCl/Cl_y ratio was near unity. Some denitrification also was observed. Low ozone was attributed to catalytic loss from enhanced ClO earlier in the winter. When recovery begins with significantly depleted ozone levels, the formation rates of higher oxides from NO_x are slowed and the production of HCl is favored over that of $ClONO_2$ in the Cl_y reservoir. The recovery of this processed air will be examined qualitatively and quantitatively using the available data from the ER-2 and contrasted to recovery in air that has not undergone ozone depletion. Our understanding of how vortex air recovers from the

perturbations caused by heterogeneous processing in polar winter is an important aspect in the assessment of continued aircraft operations in the stratosphere.

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Tropospheric Ozone Studies Using TOMS, SBUV, and Other Datasets

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Research Objectives

We have developed a methodology that can be used to determine the distribution of the integrated amount of ozone in the troposphere through the simultaneous measurements of total ozone from the Total Ozone Mapping Spectrometer (TOMS) and the integrated amount of ozone in the stratosphere from Solar Backscatter Ultraviolet (SBUV) satellites. The purpose of this research is to examine the utility of this derived quantity, called the tropospheric ozone residual (TOR) for use in various atmospheric studies. To validate this technique, we compare the TOR with ozonesonde data, selected case studies for which extensive *in situ* ozone measurements exist, and surface ozone measurements over various spatial and temporal scales.

Summary of Progress and Results

At the beginning of this research biennium, our research focused on improving the TOR methodology which had proven so successful for determining the climatological distribution of tropospheric ozone [Fishman *et al.*, 1990, *J. Geophys. Res., 95*, 3599]. That study used coincident measurements from TOMS and SAGE (Stratospheric Aerosol and Gas Experiment). To produce the TOR for non-climatological time scales, it was clear that a new initiative was necessary to extract additional information from databases that had previously not been exploited.

Over the past two years, we have focused on the potential use of SBUV data in conjunction with the TOMS data to extract tropospheric ozone information. The primary disadvantage of using SBUV measurements is the lack of vertical resolution.

On the other hand, we have shown that complete global coverage of the stratospheric overburden can be obtained with SBUV using a 5-day running average, which is a vast improvement over the temporal resolution of SAGE which requires ~40 days to obtain global coverage. We have shown that the use of SAGE data to derive TOR distributions for non-climatological time scales also introduces a high degree of aliasing into the calculated stratospheric overburden. Using the TOMS/SBUV technique, we can show reasonable agreement with the observations, but the resultant distributions must still be used judiciously and cannot be reliably compared with some surface observations. Again, however, the degree of agreement is shown to be dependent on the averaging of both the TOR and the datasets to which the TOR are being compared.

Another focus of the research is to use the TOR in conjunction with a comprehensive set of airborne measurements in tropical regimes to define regional distributions of tropospheric ozone. Our research shows that there is generally very good agreement between the spatial gradients determined from the TOR and the in situ observations. The agreement is especially good over ocean and gradients over spatial scales greater than 1000 km are very well defined by the TOR. The agreement between the TOR and *in situ* measurements over land surfaces is not as good and even appears to be poor in regions where aerosol loading in the lower atmosphere is high (e.g., in the vicinity of intense biomass burning).

A new version of the TOMS data archive has recently been released (March 1996) and we plan to carry out our research using this updated release. Some of the weaknesses we have uncovered in the TOR have been shown to be a result of some of the assumptions used to process the total ozone data in the previously archived TOMS data. The use of the recently released TOMS data should improve some of the shortcomings that we had identified in our production of the TOR.

Publications

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SBUV, GOME, and UVISI Data Analysis

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Research Objectives

To develop methods to compare remote sensing data from multiple satellite platforms. The primary focus is on ozone retrievals for both total column and the ozone vertical profile. Recently, methods have been developed to compare other geophysical parameters such as tropospheric aerosol optical depths derived from backscattered ultraviolet measurements.

Summary of Progress and Results

SBUV: In February 1987, the SBUV instrument developed an instrumental problem that significantly affected the quality of the ozone data. A method was developed to partially correct the radiance data for the effects of this instrumental problem. The Nimbus 7 SBUV data was reprocessed with this correction method and the Nimbus 7 SBUV data was released for general use. The characterization of the Nimbus 7 non-sync data is complete. The non-sync correction algorithm was published in JGR. The corrected SBUV data has been combined with the NOAA 11 SBUV/2 data to make the long-term ozone dataset used in the UNEP/WMO *Scientific Assessment of Ozone Depletion: 1994.* This combined dataset is now the standard dataset for calculating the long term trends in total column ozone and trends in the ozone profile above 25 km. With the completion of the algorithm paper and the acceptance of the corrected SBUV dataset by the scientific community, the work done by this RTOP will shift to the analysis and characterization of other satellite ozone datasets.

GOME: The ESA GOME instrument, on ERS-2, was successfully launched in Spring 1995. Although the GOME instrument uses the same backscatter ultraviolet physics as the SBUV/TOMS, it uses a different instrumental configuration. The GOME instrument has continuous coverage from 240 nm to 810 nm, at 1 nm resolution, compared with the SBUV wavelength coverage, 250 nm to 340 at 12 wavelengths.

We have used the NASA/Goddard Space Flight Center algorithms for calculation of the total column ozone using GOME radiance and irradiance data. This ozone product will be referred to as GOME-TOMS. This processing was done to check the GOME radiance/irradiance calibration and to test the systematic assumptions in the ESA DOAS algorithm. GOME-TOMS will not replace the ESA ozone processing.

There is overall reasonable agreement between the GOME-TOMS and the GOME-DOAS. The GOME-DOAS results are consistently lower that the GOME-TOMS results. The GOME-DOAS ozone values show a 'step function' behavior when plotted as a function of latitude. This is probably the results of some assumptions in the GOME-DOAS retrieval algorithm. GOME-TOMS - GOME-DOAS differences show a significant (0 to 10%) latitude dependence. This is probably easier to interpret as a solar zenith angle dependence. As the TOMS algorithm has not shown this solar zenith angle dependence using the Nimbus 7 radiance data, one must assume that this solar zenith angle (SZA) dependence is contained in the GOMS-DOAS data. The other notable feature is the scan angle dependence of the GOME-TOME results. Further studies are required to assess the cause of this scan angle bias.

The GOME studies are ongoing. ESA views the GOME-TOMS/GOME-DOAS comparisons as a critical validation step in the acceptance of the GOME data.

MSX UVISI: The UVISI instrument on the MSX satellite was launched on 24 April 1996. The instruments are operating and the production of level 2, (calibrated radiances) is still ongoing. UVISI data have not been released.

Publications

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Theoretical Studies of Polar Stratospheric Clouds and the Background Sulfate Aerosol

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Research Objectives

The purpose of the research project was to carry out a series of theoretical studies to better understand the formation of stratospheric aerosols and polar stratospheric clouds and how they are involved in ozone depletion. Among the studies that were proposed were: the development of techniques for studying heterogeneous processes on nitric acid polar stratospheric clouds; the development of models to analyze lidar returns from polar stratospheric clouds; studies of microphysical processes in volcanic plumes; an analysis of phase diagrams for stratospheric particles; and a study of ternary system particle formation in the polar stratosphere.

Summary of Progress and Results

The main goals of the proposed work were accomplished and papers were prepared and submitted for publication in appropriate journals. Perhaps the most important product generated during the course of the study was a one-dimensional model for ternary system polar stratospheric clouds. This model begins with the background sulfate aerosol and using basic microphysical concepts determines the size distribution of the ternary system particles as a function of altitude. Since the model yields sizes, composition, and vertical location of the particles it can be used to study heterogeneous chemical processes taking place on the surfaces or the interiors of ternary system polar stratospheric cloud particles. The results from the model were used in a Mie scattering code to determine extinction and backscatter. The extinction values were compared with those measured by the SAM II satellite system. These results were presented in a recent paper published in *Geophysical Research Letters*. The model has been adapted to include a wider range of environmental parameters and to simulate lidar backscatter profiles from polar stratospheric clouds in the stratosphere and from water ice clouds in the troposphere.

The analysis of microphysical processes in volcanic clouds was carried out and the results are described in a paper accepted for publication. Other interesting facets of the problem became apparent during the course of the work and follow-on studies are being carried out. This microphysical model is intended to be used in conjunction with plume dispersion models developed at NASA Ames Research Center.

The analysis of particle formation processes was presented in a paper co-authored by my student Mr. Terry Olson. The theory gives nucleation rates in excellent agreement with experiment. The

generalization to multi-component aerosols is the logical next step in the development of this theory. Studies of nucleation of sulfate particles near the tropical tropopause were carried out in collaboration with Dr. C. Brock of the University of Denver. The results were published in a paper in Science and describe a tropical source for the stratospheric aerosol. A study of the phase diagrams for nitric acid solid phase aerosols was carried out with my student, Mr. J. Benjamin. The results were presented at the American Geophysical Union meeting as well as at a High Speed Research Program (HSRP) meeting. Other research activities included participating in the NASA Antarctic aircraft flights staged from New Zealand as part of the ASHOE-MAESA program and serving on the theory team for the SPADE (Stratospheric Particle and Dynamics Experiment) campaign.

Publications

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Improving Vertical Transport in Chemical Transport Models: Data and Model Analysis

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Research Objectives

The main goal of this startup project has been to assess the feasibility of using available field data to improve the current understanding of the processes that control vertical transport of chemical constituents in the real atmosphere in order to better address the simulation of these processes in chemical transport models (CTMs). More accurate simulations are becoming necessary as we try to simulate tracers for inverse modeling studies and to study shorter-lived photochemically active gases. One movement towards addressing this need is the development of high resolution transport models driven by observed wind fields. However, even these models will rely heavily on the parameterizations used for boundary layer mixing and convective transports. The roles of these transport processes are still not well understood in terms of regional or global budgets. One of the problems in improving the simulations is a lack of compiled data for model comparison. In this study, we attempt to provide a basis for evaluating model convective schemes by compiling specific observed vertical profiles of trace gases for direct comparison with profiles generated in CTMs.

Summary of Progress and Results

To address our objective of compiling observed vertical profiles to be used to improve CTMs, we used data collected from the Global Tropospheric Experiment (GTE) to amass vertical profiles of carbon monoxide, CO, in different regions and under different meteorological conditions. From this data we have compiled vertical profiles from 15 distinct regions.

Results so far confirm several characteristics in these profiles. The equatorial regions provide the most information. In this area a dominant intrusion of air around 2 to 4 kilometers occurs in several regions. The most notable intrusions occur in equatorial Africa and Atlantic. An intrusion of very high concentration air is seen over equatorial Africa a little below two kilometers and is evident up to around 4 kilometers. A similar intrusion occurs in the equatorial Atlantic. It begins around 1.5 kilometers lasting until 3.5 kilometers. These low-level intrusions are also evident in the Pacific from the Central Equatorial Pacific Experiment (CEPEX). While the GTE profiles suggest the cause could be convective activity or a boundary layer phenomena, the CEPEX results suggest possible stratospheric influence due to high ozone and low relative humidity observed there.

Equatorial Africa contains an important result for confirming model trace gas profiles. Considering the overall and daily profiles a lull is evident at about 5 to 7 km. The concentrations in this region

are substantially less variable than the concentrations just above and below it staying right at 100 ppbv CO. The concentrations otherwise fluctuate by at least 50 ppbv.

A land versus ocean graph of equatorial Africa, concludes that although the surface concentrations over land differ from over the ocean the remainder of the profiles are similar with the lull being more apparent over land due to the intrusion. The intrusion of high concentration ('dirty') air occurs from 2 to 4 km, below the lull region. There the concentrations are well above normal at 300 to 700 ppbv CO.

The equatorial Central Pacific contains a wide variety of concentrations. Yet the individual profiles seem to stand out as smooth profiles. Thus, one characteristic concentration does not hold due to the variations in concentrations between longitudes but the general profiles are similar.

The mid-latitude profiles are less stable and more dependent on synoptic activity than the tropics. Two major differences include faster mixing and no strong intrusion. In mid-latitude Africa there is no lull at mid-levels as in Equatorial Africa. As is true for most of the mid-latitude profiles they are generally more homogenous but can change rapidly due to meteorological conditions. Over the Northern Pacific there is evidence of forest fire influence on the CO concentrations. This appears to play a significant role in creating high CO concentrations over the Aleutians. However, only lower altitudes are available at this location. The polar regions represent much cleaner air, but both the Arctic and Greenland profiles do have intrusions of higher concentrations in the higher altitudes (4 to 6 km). Arctic Haze may be the explanation for this increase. Previous studies have attributed an increase in concentration around 4 to 6 km in the polar region to Arctic Haze.

Through this work, we find there are enough observed vertical profiles that more detailed comparisons can be done to models. This work establishes a basis for a more comprehensive comparison of a model simulation to observations in many different regions around the globe. We find that the equatorial regions show more consistent patterns such as the mid-level lull and low-level intrusions. In the mid-latitude regions, model comparisons should be done under different synoptic conditions. However, there still needs to be more work to understand the processes that cause the equatorial phenomena like the low-level intrusion and mid-level lull.

Publications

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Volcanic Aerosol Properties from Nimbus 7/TOMS and Meteor-3/TOMS Ultraviolet Radiance Measurements and Their Effect on Stratospheric Ozone

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Research Objectives

The key research objective is the determination of the properties and atmospheric effects of aerosols injected into the stratosphere after volcanic eruptions. The research is based on data obtained from the Nimbus 7/TOMS, Meteor-3/TOMS, Nimbus 7/SBUV, NOAA 11/SBUV, and the SAGE-II instruments (Total Ozone Mapping Spectrometer, Solar Backscatter Ultraviolet spectrometer, and Stratospheric Aerosol and Gas Experiment). The work in this area, not supported by the ozone measurement program, will yield information on the latitude distribution of stratospheric aerosols as a function of time after volcanic injection. The properties that can be deduced from the ultraviolet backscattered radiation are: 1) mean particle size, 2) optical depth, 3) height of the aerosol density maximum, and 4) the error introduced into the ozone measurements. The research will provide a means of correcting the total ozone measurements for TOMS and SBUV, and correcting the SBUV ozone profile data during periods of stratospheric aerosol contamination. The results will increase the accuracy of long-term ozone trend determination. By determining the time and space distribution of aerosols, this study will aid in understanding the effects of heterogeneous chemistry reactions involving sulfate aerosols on high-latitude ozone depletion. Additional studies are to be performed on tropospheric absorbing aerosols to establish the feasibility of detecting them using TOMS radiance and irradiance data.

Summary of Progress and Results

The cross-track scanning capability of TOMS radiance measurements was used to deduce the phase function characteristics of the H_2SO_4 - Water aerosols that were injected into the lower stratosphere after the Mt. Pinatubo eruption in June 1991 and after the eruption of El Chichon in 1980. Papers were produced that gave the 1) mean particle size, 2) optical depth, 3) height of the aerosol layer, and 4) the error introduced into the ozone measurements. In addition to meeting the main objectives of the proposed research, the following key points were obtained: 1) The time history of stratospheric aerosol decay after an eruption; 2) a means of correcting the TOMS measurements for errors introduced by the stratospheric aerosols; and 3) comparisons with ground based and *in situ* measurements to establish the validity of the results. Additional research was conducted to establish

the possibility of using TOMS data for detecting absorbing and non-absorbing aerosols in the troposphere during all months of the year. It has been determined that TOMS can detect aerosols over both land and water (smoke, dust, volcanic ash, and sulfate aerosols) and determine their daily flow patterns. These results have been published with additional work in progress from the follow-on research effort. During the 1994 to 1996 period a program of joint research with other groups has been set up to provide ground-based validation of the satellite observations.

Publications

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European Space Agency's ERS-2 Global Ozone Monitoring Experiment, Calibration, Validation, and Research

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Research Objectives

The purpose of this research is to conduct investigations with the European Space Agency's (ESA) ERS-2 Global Ozone Monitoring Experiment (GOME) high spectral resolution Earth albedo data. This effort complements research with SBUV, SBUV/2, SSBUV, and TOMS data (henceforth called BUV instruments). The investigations conducted with GOME data consist of four tasks: 1) Pre-launch calibration evaluation, 2) Post-launch data validation, 3) Algorithm research, and 4) Tropospheric ozone studies. The initial studies focused primarily on analysis solar irradiance, backscattered radiances (Level 1 data), and total ozone (Level 2 data) from GOME Channels 1 and 2. These channels cover the wavelength range 240 to 405 nm which overlaps wavelengths covered by the SBUV and TOMS instruments. Our goal is to develop a consistent, long-term, global ozone dataset through better understanding of instrument performance and atmospheric radiative transfer particularly in the ultraviolet and visible. Our initial results using BUV radiance and irradiance observations and radiative transfer models showed some GOME calibrations errors which have little effect on total ozone values but larger effect on ozone profiles. GOME radiances processed through the BUV algorithm solar showed some solar zenith angles dependencies in the GOME total ozone retrievals.

Summary of Progress and Results

The Goddard validation effort began before the launch of GOME. NASA standards used for calibrating SBUV/2 and TOMS were used to calibrate GOME. These calibrations were compared with the ESA calibration and agreement was found to be better than 3%. The good agreement among the various calibration techniques provides confidence that the GOME instrument and the US BUV instruments are on a common radiometric scale, traceable to NIST standards, and provide a solid baseline for inter-comparisons of these measurements from space.

Once GOME was launched, the ESA organized a validation effort which included several research institutions throughout Europe and the United States including this Goddard group. The Goddard validations plans included intercomparisons with Earth Probe TOMS and NOAA 14 SBUV/2. Because of the TOMS launch delay, and operational problems with SBUV/2 the validation activity was limited. ESA processed and released for validation approximately 15 days of GOME data covering the period August 1995 to January 1996 which included overlap with SSBUV-8 flown in January, 1996. In addition to the SSBUV data, a limited SBUV/2 dataset was validated for comparisons with GOME data.

With the limited datasets, a great deal was learned about the initial performance of GOME. GOME data were reprocessed incorporating improvements as result of the first validation period. Level 1 solar irradiance comparison demonstrated a large wavelength dependent change in GOME sensitivity, resulting from the space vacuum, to be of the order of 15% at 300 nm. Most of this error has been removed with corrections based on reanalyzed vacuum calibration data. The solar irradiances now agree with SSBUV and the UARS SOLSTICE solar irradiance data to about 5%.

Normalized radiance or directional albedos (henceforth called radiances) between satellites are not easily comparable because of small wavelength and solar zenith angle differences and imperfect scene matchups. Therefore radiances between satellite instruments were compared in the following way. Radiance were computed from the US BUV instruments derived ozone values coincident with GOME radiances using the BUV radiative transfer model at the GOME solar zenith angles and reflectivities at 380 nm and then compared to measured GOME radiances. An example of these comparisons is shown in Figure 1. The GOME radiances agree with SBUV/2 calculated radiances to 5% or less at wavelengths larger than 310 nm primarily used for total ozone retrievals. At wavelengths shorter than 300 nm, GOME radiances appear to be high by as much as 10%. The SBUV/2 have been independently validated which gives confidence to the credibility of the comparisons. Similar results were found using SSBUV-8 data. The fine structure seen in this Figure 1 results from the Ring effect which is not included in the model but appears in the GOME data.

The GOME derived total ozone data products, using the DOAS technique, were compared with GOME total ozone values derived from radiances, at the BUV wavelengths longer than 310 nm, processed through the TOMS algorithm. The difference demonstrated solar zenith angle and small scan angle dependencies. Further discussion of these results appear in the Research Summary prepared by James Gleason of Goddard Space Flight Center.

A similar test was performed to test GOME ozone radiances at wavelengths shorter than 310 nm which are used for profile retrievals in the stratosphere. GOME has not yet produced an operational ozone profile product for comparisons. GOME radiances at the BUV profile wavelengths were processed through the SBUV algorithm and compared with climatological ozone values from SBUV/2 for the same season and latitude (no concurrent SBUV/2 data are available yet). Comparison of ozone amounts are illustrated in the upper panel of Figure 2. The differences, shown in the lower panel, range from 10 to 30% low. Radiative transfer predicts a 1% radiance error results in a 2% ozone error at 1 mbar and practically no error near 10 mbar. Differences in ozone amounts shown in Figure 2 are consistent with the wavelength dependent radiances differences shown in Figure 1.

The irradiance error which results from the air-to-vacuum sensitivity change, discussed earlier, likely appears in the radiance as well. If this is the case, this error is canceled in the normalized radiances (albedos) and has no effect on ozone retrievals. Therefore the error seen in the radiances from the BUV comparisons below 300 nm is an unaccounted for calibration error. The source of the error remains unknown but is being investigated.

Algorithm research using GOME radiances has begun. Initial research included studies of the Ring effect and its relationship to cloud top heights, but are not reported here. GOME radiances between 340 and 400, which are free from ozone absorption, were used to further study reflectivity anomalies discovered in TOMS associated with absorbing aerosols such as smoke and dust. The initial release of GOME data demonstrated that these aerosol signatures also appear in the GOME radiances however further validation using the TOMS Earth Probe is required to draw any conclusions at this time.

A more detailed discussion of the GOME validation effort summarized here appears in ESA Report WWW 108, May, 1996.

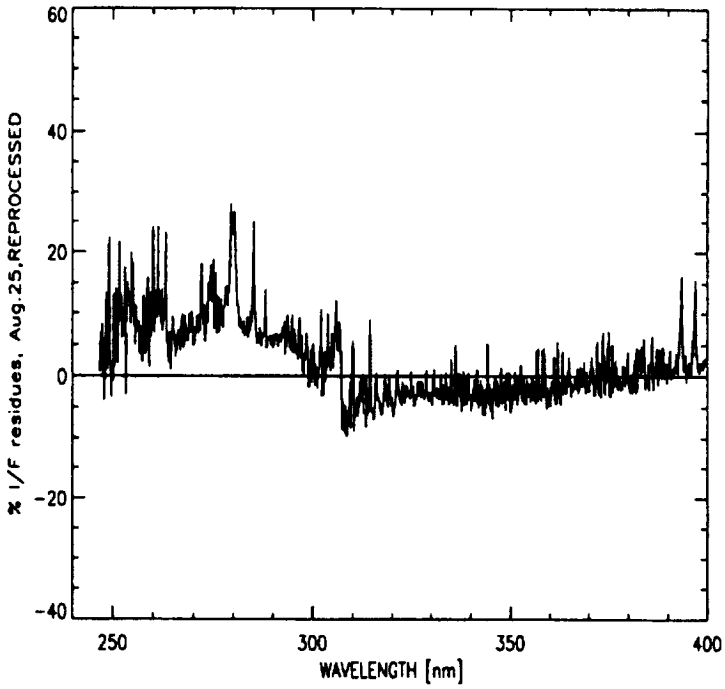

Figure 1. Comparison of measured GOME radiances with computed radiance derived from SBUV/2 ozone data.

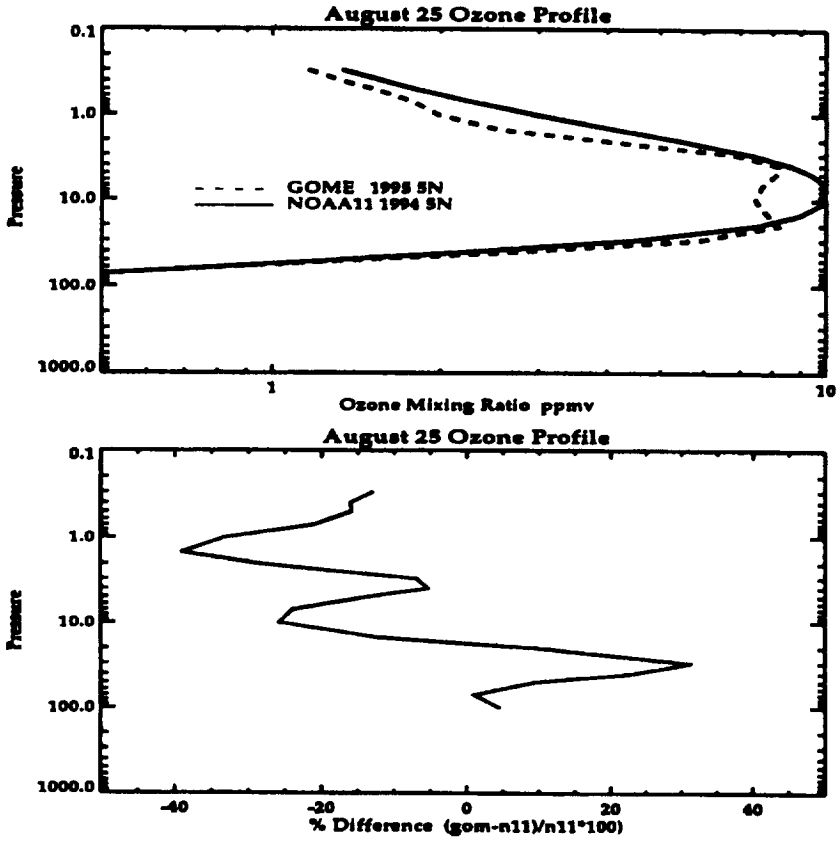

Figure 2. Profile comparisons between GOME and SBUV/2. Upper panel are ozone amounts. Lower panel is (GOME-SBUV/2)/SBUV/2x100.

Publications

None

Dynamical Studies Using STRAT Data

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Research Objectives

This work focuses on the following questions relevant to transport of chemical constituents across the subtropical lower stratosphere:

1. What are the preferred longitude bands for exchange of air between the tropics and extratropics?
2. What determines the strength of constituent gradients often seen in the subtropics?
3. What role do gravity waves play in vertical and horizontal transport in this region?

Specific tasks include:

- Diagnose the seasonal distribution of continental scale features in the tropics/subtropics using ECMWF and SAGE data.
- Plot all constituent profiles for every ER-2 flight crossing the subtropics for STEP, AAOE, AASE 1 + AASE 2, SPADE, ASHOE/MAESA, and STRAT.
- Define stratospheric air masses by their chemical properties.
- Define locations of air mass boundaries and quantify magnitudes of tracer gradients across them.
- Plot correlation diagrams for constituents versus wind and potential vorticity (PV) and for gradients of constituents versus gradients of wind and PV.
- Carry out power spectral analyses of ER-2 variables along flight tracks to characterize sub-planetary scale motions.
- Carry out numerical simulations using the University of Wisconsin Non-hydrostatic Modeling System (UW-NMS) for specific ER-2 campaigns.
- Compare UW-NMS trajectories and tracer distributions with ER-2 data.
- Diagnose transport associated with convectively excited gravity waves in the UW-NMS.

Summary of Progress and Results

ECMWF analyses, SAGE aerosol, and UW-NMS simulations illustrate that there are preferred longitude bands of meridional exchange across the subtropics near 20 km. These seasonal "conveyor belts" into and out of the tropics occur in the vicinity of the continental scale anticyclones, which decay upward from tropospheric monsoon structures. In regions removed from these anticyclones, such as the central Pacific, pronounced "jumps" in trace constituent values are more frequently observed by the ER-2.

The most popular current descriptor of these regions of enhanced constituent gradient is "transport barrier". Since enhanced gradients of potential vorticity (PV) are often co-located, inhibition of Rossby wave breaking, and the consequent reduction in mixing, has been suggested as a dynamical explanation. Yet at scales below about 1000 km, the Rossby wave propagation mechanism becomes less robust and differential advection more readily leads to a folding of PV contours. It is shown that an enhanced PV gradient requires transport; such a region cannot be a minimum in flux or net flux. It is further argued that at scales below 1000 km both PV and constituents are advected rather passively. A corollary is that enhanced PV gradients on the flanks of a Rossby wave breaking zone are not the primary determinant of mixing breadth. More fundamental controlling processes include where the extratropical Rossby waves grow, their refraction geometry, and the locations of critical surfaces.

A variety of studies have recently shown that a broad spectrum of gravity wave activity is found across the lower stratosphere, maximizing in the tropics. Moreover, ER-2 meteorological and constituent data do not show variance minima near the constituent jumps. In the absence of evidence that there is any suppression of synoptic/mesoscale mixing processes, instead of "transport barrier", we suggest the meteorological descriptor "air mass boundary". As in the troposphere, air mass boundaries are quite active mixing zones. Trajectories from the UW-NMS for the 24-28 March 1994 ASHOE/MAESA campaign suggests that the magnitude of the jump in constituent concentration is controlled by a competition between confluence (driven by 3-D large scale differential advection) and synoptic/mesoscale mixing (which is rather homogeneous).

Publications

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Studies of Middle Atmospheric Radiative, Photochemical, and Dynamical Processes Using Satellite Data

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Research Objectives

- Observationally determine the components of interannual ozone and temperature change in the stratosphere during the period since 1978 when continuous satellite measurements have been available.
- Investigate the relative importance of chemical, dynamical, and radiative processes in producing the observed lower stratospheric ozone and temperature trends.
- Investigate the nature of the solar cycle variation of the stratosphere using both statistical and modeling methods.

Summary of Progress and Results

- The observed longitude dependences of total ozone and lower stratospheric temperature trends in the northern winter were found to be similar and to vary significantly from month to month. Comparisons with radiative model calculations showed that it was difficult to explain these characteristics by radiative processes alone. Using a mechanistic ozone transport model together with NMC geopotential height data, it was shown that most or all of the statistically derived longitude dependence of the observed ozone trends can be explained as due to decadal changes in the amplitudes and phases of quasi-stationary Rossby waves originating in the troposphere. Assuming that the observed lower stratospheric temperature trends in the northern winter are dominantly forced by dynamical processes (driven by decadal tropospheric climate change), an upper limit on the contribution of dynamical forcing to mid-latitude ozone trends was estimated. Results indicate that dynamical forcing can contribute a major fraction of zonal mean ozone trends at latitudes up to 40°N during the northern winter.

  At latitudes poleward of 50°N, the dynamically forced trend component is small compared to that due to heterogeneous chemical forcing. Our preliminary conclusion is that long-term variations in lower stratospheric circulation, driven by decadal tropospheric climate change, are a significant source of both mid-latitude ozone trends and lower stratospheric temperature trends.

  Earlier, we investigated the alternate hypothesis that the observed temperature trends are a direct radiative consequence of observed ozone trends (assuming that the latter are entirely chemical in origin). A 1-D radiative transfer model with fixed dynamical heating was applied to calculate the latitude and seasonal dependences of expected zonal mean temperature trends using the observed

zonal mean ozone trends. Results were found to be sensitive to the assumed altitude dependence of the ozone mixing ratio trends which are not well determined observationally. Although it was possible to simulate approximately the observed zonal mean temperature trends, the fixed dynamical heating assumption is questionable in the northern winter and it was not possible to prove cause-and-effect.

- Multiple regression analyses of satellite ozone profile measurements covering a 15-year period were applied to determine the dependences on altitude, latitude, longitude, and season of the apparent solar cycle variation of total column ozone. It was found that most (> 85%) of the 1.5 to 2% solar cycle variation of total ozone occurs in the lower stratosphere (altitudes < 28 km). Evidence was obtained for a related solar cycle variation of lower stratospheric temperature (50 to 150 hPa) and geopotential height (30, 50, and 100 hPa) with geographic dependences similar to those of the solar cycle variation of total ozone. Initial calculations indicate that a 10- to 12-year dynamical oscillation of the lower stratosphere (discovered originally by K. Labitzke and H. van Loon) is mainly responsible for this decadal variation of total ozone. The apparent solar cycle variation of upper stratospheric ozone is nearly twice as large as estimates based on current two-dimensional models of the middle atmosphere. At middle and high latitudes near 4 hPa, the large amplitudes and strong latitude dependences of the estimated temperature variation suggests that changes in stratospheric dynamics over the 11-year solar cycle may also be important for understanding observed temperature and ozone variations on this time scale.

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Direct Measurements of Tropospheric Ozone from TOMS Radiances

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Research Objectives

Measurements of the global tropospheric ozone fields are of great importance for a full understanding of the chemical and dynamical processes that control the distribution and amount of trace gases in the troposphere and stratosphere. In previous work we have shown that tropospheric ozone amounts can be retrieved directly from the radiance data obtained by TOMS (Total Ozone Mapping Spectrometer), and that the use of TOMS archived ozone amounts can lead to large errors. This new algorithm was applied to the Biomass Burning regions of Africa, and daily maps of the tropospheric ozone were obtained. The specific objectives of this investigation are:

- To develop the equatorial algorithm further and to extend the analysis to cover the entire African continent
- To apply the algorithm to the study of the climatology of the biomass burning seasons
- To develop a new technique for the derivation of a climatological tropospheric ozone database using cloud to ground radiance differences, and
- To study the global trends of the zonally averaged tropospheric ozone from 1988 to 1993.

Summary of Progress and Results

In 1994, we developed a new algorithm to obtain tropospheric column ozone amounts directly from the TOMS measured albedos. These albedos are archived on the High Density TOMS data tapes (the HDT tapes). We were able to obtain maps at a spatial resolution of about 50 km square, which is ~6 times more dense than the Grid-T TOMS product. This technique was applied to the tropical eastern Atlantic, the adjacent African continent, and the Indian Ocean, during the biomass burning season in 1989. The analysis was restricted to latitudes between 10°N to 10°S, in order to minimize variations in the stratospheric ozone.

In 1995 we increased the spatial extent of the algorithm to the entire tropical zone [Kim, 1995; Kim *et. al.* 1996]. To increase the accuracy of the derived tropospheric ozone, 15-day averages of the data were examined. The initial work was performed for the month of October 1992, for which time there were extensive sonde and aircraft measurements (TRACE-A Mission). An apparent longitudinal wave-one structure was identified in the total ozone field, with a maximum at 0°

longitude, and a minimum at 180°. The peak to peak value of the wave was 13 DU. If the wave-one pattern was ascribed to the stratosphere, then good agreement was obtained between the tropospheric column obtained from our algorithm, and that derived from the sonde and aircraft measurements. It should be noted however, that this conclusion is in apparent disagreement with the profile data from the SAGE and MLS instruments. We then extended the analysis for the first fifteen days of all the months of 1992, and find that the wave-one pattern is persistent for the entire year, and comparisons with sonde data are consistent with the pattern being in the stratosphere. Preliminary data for 1990, and 1989, also show this same pattern. The next stage of the investigation will be to preform the data analysis for all months from 1978 to 1993, and to investigate the climatology and trends of the tropical tropospheric ozone. The eventual aim is to produce an archival dataset for the use of other investigators.

The methods described above work only in the tropics, where the stratospheric field is smooth and can be assumed to be only a function of latitude. This is not true at mid- to high-latitudes.

We have been investigating another method, which looks at radiances obtained above clouds with a large enough dimension to fill the field of view of TOMS, and those obtained from a contiguous pixel of clear sky, or a cloud at a different altitude. Calculations have shown that the ratio of the radiances is relatively independent of the stratospheric column, thus obviating the need for accurate estimates of this quantity. To perform a preliminary analysis of the method, we obtained a sample of data from the new high resolution ISCCP cloud dataset. The month we selected was October 1990, and we chose the geo-synchronous satellite which was centered over the Mid-Atlantic, i.e., a period which should correspond to the biomass burning season. This should maximize our chance of seeing tropospheric ozone. We have generated a new set of look-up tables based on the DISSORT radiative transfer code. The biggest difficulty has been to identify those pixels with total cloud cover., for a low reflectivity total cloud could just as well be a partial cloud with high reflectivity.

However preliminary results are encouraging. We have developed a method to use the visible and infra-red optical depths given in the ISCCP dataset to aid in this identification. The tropospheric column results that we are deriving, are consistent with those obtained from the method discussed in previous paragraphs. However, the method still shows a wide scatter in the results.

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Isentropic Analysis and Modeling of the Southern Hemisphere Circulations and Exchange within the Wintertime Stratospheric Vortex

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Research Objectives

The principal goals of this research were to:

- provide on-site forecasts of isentropic atmospheric structure and circulation in support of ER-2 flights during the Intense Observation Periods (IOPs) of the 1994 Airborne Southern Hemisphere Ozone Experiment/Measurement for Assessing the Effect of Stratospheric Aircraft (ASHOE/MAESA) program;
- study the role of amplifying baroclinic waves in the stratospheric extrusion of ozone, the transport of dehydrated polar air into lower latitudes and the intrusion of tropospheric water vapor into the stratosphere; and
- investigate the capabilities of numerical models based on different numerical schemes and coordinate systems to conserve atmospheric properties, especially ozone and water vapor.

Summary of Progress and Results

The primary means to address the above goals were through use of the University of Wisconsin (UW) hybrid isentropic-sigma (θ-σ) coordinate numerical weather prediction model. During the IOPs of ASHOE/MAESA, the UW θ-σ model provided 0 to 84 hour forecasts of isentropic atmospheric structure and processes in support of ER-2 flights for operational activities in Christchurch, New Zealand. The UW θ-σ model utilizes sigma coordinates to describe the lowest 150 millibars (mb) of the atmosphere and isentropic coordinates to describe the free atmosphere. Predictions of the tropospheric/stratospheric distributions of winds, temperature, water vapor, potential vorticity (PV) and corresponding isentropic transport processes were provided daily.

After completion of the IOPs, a study of the impact of baroclinic wave amplification on the forcing of extrusions of high PV air and trace constituent transport from within the stratospheric vortex to lower latitudes and elevations was initiated. The isentropic structure of meridional transport processes revealed that the equatorward transport of high PV in filaments between 340 K and 400 K was coupled with baroclinic development [Johnson *et al.*, 1996]. The filamentary structure of high PV lies within the trough of a baroclinic wave and extends vertically from the tropopause to the level where the zonal temperature gradient vanishes. With a reversal of the zonal temperature gradient at

the tropopause, the meridional winds of the lower stratosphere weaken with height; a condition that caps the PV filament and its equatorward displacement. This structure is consistent with concepts of stratospheric extrusions associated with tropopause folding and accounts for the interchange of trace constituents across the lateral boundary of the wintertime stratospheric vortex.

The relative capabilities of isentropic and sigma coordinate models to conserve joint distributions of PV and trace constituent transport were investigated for an ASHOE IOP using simulations from the UW θ-σ and σ coordinate models and the National Center for Atmospheric Research (NCAR) Community Climate Model (CCM2). An initial proxy distribution of ozone (O_3) was specified analytically as a function of the initial PV on each model level. The capability of a model to retain a correlation of unity through the integration is a measure of its predictability of transport processes within the atmospheric continuum. At and above 370 K, the UW θ-σ model correlations remained above 0.99 throughout the 10-day simulation while correlations in the UW σ model simulation decreased to 0.50 by day 10 in the lower stratosphere. Simulations from CCM2, a state of the art climate model, had correlations near 0.95 in the low stratosphere at day 10. However, the correlations in the upper troposphere were substantially reduced in CCM2 compared to the UW θ-σ model. These results, presented in Zapotocny *et al.* [1996a], document the superior conservation characteristics in the upper troposphere and lower stratosphere of models based on isentropic coordinates.

A second experiment examined the capabilities of models to conserve equivalent potential temperature (θ_e). Non-conservation of θ_e constitutes an error that seriously degrades a model's ability to simulate the full range of hydrologic processes. The initial θ_e distribution from the same IOP data as above was inserted as a trace constituent in all models. The models were then integrated to 10 days and conservation examined. Similar to the proxy O_3 results, correlations remain higher in the UW θ–σ model than in the other two models. Results from this experiment are presented in Zapotocny *et al.* [1996b].

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Use of Existing Radionuclide Databases in the Development and Verification of Global 3-D Chemical Transport Models

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Research Objectives

Because the global source strength of atmospheric radon is reasonably well known, and its loss term limited to its own radioactive decay (occurring with a half-life of 3.8 days) comparisons of predicted and observed distributions of atmospheric radon have gained increasing recognition as a standard test of the performance of the transport component of global and regional 3-D models. The goal of this research program is to work with interested modeling groups to expedite and facilitate such comparisons, in order to: 1) identify specific areas of weakness; 2) improve model transport parameterizations; and 3) provide a quantitative demonstration of model performance. The basic idea is to introduce radon source and decay terms into the models, and then compare the resultant predicted atmospheric radon distributions with available observations. Significant disagreements between the predictions and the observations not only point up shortcomings in the model's representation of transport, but also provide information on which model parameterizations need improvement. Good agreement, on the other hand, is strong evidence that the model is handling transport correctly, allowing us to proceed with increased confidence to address the equally difficult chemical component of the problem. Our own extensive inventory of airborne radon measurements, as well as surface-level observations made by other groups have been used for this purpose.

Summary of Progress and Results

A primary activity in this project has been to advocate and facilitate the use of comparisons between model-predicted and observed atmospheric radionuclide distributions, in conjunction with the global 3-D models used by the Global Modeling Initiative (GMI) in preparing the First Interim SASS Assessment. Both chemical and transport processes are accounted for in the GMI models. For example, in assessing the effect of aircraft effluents on the chemistry of a given region of the upper troposphere a model must keep track not only of the chemical reactions of effluent species emitted by aircraft flying in that region, but also the transport into and out of that region of these and other chemically active species. These include the effects of vertical convective transport of pollutants from the boundary layer, the long-range transport of chemical species from both distant and nearby regions of the troposphere, and intrusions of stratospheric air.

The radionuclides considered for these comparisons are ^{7}Be, ^{32}P, ^{222}Rn and ^{210}Pb. Thus far attention has focused on ^{222}Rn (radon) and comparisons of model predictions with ground based and free tropospheric radon observations made over the period 1975-1994.

To facilitate these comparisons I have made available to the GMI Team all of the published and unpublished radon data acquired by our group, and worked with Team members on the evaluation and application of airborne and surface-level data from other sources. I have also worked with the natural radionuclide component of the IGAC Global Emissions Inventory Activity (GEIA), and with Steve Schery of the New Mexico Institute of Technology on a reassessment of the global radon source function used in the model calculations. As a result of these activities a preliminary version of a revised source assessment was made available to the GMI Team. While far from complete and not ready for release, it did permit a first-cut estimate of the potential effect of uncertainties in the radon source function on the model-observation comparisons.

An important component of the tests of the CCM2, UCI and IMAGES models used in the Interim Assessment are comparisons between the predictions of these models and the set of 22 radon profiles acquired by our group on flights out of Moffett Field, CA in the summer of 1994. Figure 4-7 of the First Interim SASS Assessment plots those calculations against these observations.

All three models do a reasonable job of reproducing the observed mean profile in the 4 to 10 km region. Agreement is not so good in the 2-4 km interval, though this may be due, at least in part, to model artifacts arising from continental edge effects.

Most significant, however, is the failure of all three models to capture the change in slope and the factor of two increase in mean radon concentrations observed between 11 and 13 km. Meteorological analysis (Kritz *et al.*, Tellus 42B, 46-61, 1990) has shown that similar high upper tropospheric radon concentrations observed near Hawaii and over the eastern Pacific near California resulted from the convective uplift of radon-rich Asia boundary layer air followed by rapid eastward transport in the polar jet. (This process would of course result in a similar transport of many chemically active species as well.) I would venture the personal opinion that the disparity between observed and predicted upper tropospheric radon concentrations arises from shortcomings in the model representations of convection (at least in Asia), and possibly in the representation of the long-range trans-Pacific transport as well.

An important aspect of the activity outlined above, and my attendance at and participation in the GMI Team meetings and assessment process (made possible by the funding provided by this project) is that it has given me an opportunity for regular, formal contact with a wide range of modelers and modeling groups. This has not only enabled me to gain a better awareness of current problems and trends in model development, but has also been of material value in the planning of the field measurement campaigns carried out by our group---such as the mid-continental flight series we carried out in the summer of 1996.

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TOMS Ozone and Sulfur Dioxide Analyses

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Research Objectives

The capability of the TOMS instrument to detect the presence of volcanic eruption clouds by virtue of their sulfur dioxide content, and to measure the mass of sulfur dioxide in the clouds over 4 orders of magnitude, is a powerful tool to evaluate volcano-climate relations. Our objective is to measure volcanic eruption sizes in the TOMS dataset with documented accuracies for analysis of climate effects and as a basis for refining the historical (pre-TOMS) record of eruption sizes. The retrieval algorithm was analyzed with simulated radiances and found to have reasonable fidelity if no ash was present in the volcanic cloud. However, ash at moderate optical depths produces errors up to 30%. An improved algorithm which retrieves accurate ozone and ash type and optical depth in addition to sulfur dioxide is being tested prior to implementation in processing of new Earth Probe TOMS and ADEOS TOMS data by our group. We have improved public access to our volcano data by construction of a WWW page. Finally, we have supported an effort by the FAA and NWS to collect Earth Probe TOMS data in real-time for volcanic hazard mitigation in Alaska, and are assisting NOAA/NESDIS and NCAC/USGS in accessing near real-time TOMS data for global assessment of volcanic hazards.

Summary of Progress and Results

Our research has focused in the following areas:

- Analysis of volcanic eruptions during the 14.5-year data record collected from the Nimbus 7 TOMS, and the 3.5-year record of Meteor-3 TOMS. Over 100 eruptions were observed during

the TOMS data record. The largest (20 Mt sulfur dioxide) was Mt. Pinatubo in June 1991, followed by El Chichon (7 Mt) in April 1982. Five others produced more than 1 Mt (Sierra Negra, Nyamuragira - the Mystery volcano of 1981), Mauna Loa, and Cerro Hudson). We found that the potential for climate impact depended significantly on whether the eruption was explosive or effusive. Explosive eruptions exhaust their sulfur dioxide in one or two brief bursts but put significant amounts of sulfur dioxide in the stratosphere where it remains for a year or two; however, effusive eruptions can continue for weeks, months, or years, generating short-lived sulfate in the troposphere with potential for climate effects as long as the eruption continues.

- Evaluation of errors produced by the existing algorithm for discrimination of sulfur dioxide from ozone in the TOMS data. The Version 6 algorithm for evaluating sulfur dioxide was developed in 1983. Although it had known artifacts, such as an unstable background level, it was believed to have errors less than 30%, a level significantly better than other methods for determination of volcanic output, and suitable for climate studies which were accustomed to order-of-magnitude measures of volcanic input to the atmosphere. An evaluation of the algorithm errors became possible when a radiative transfer specialist joined our group in 1993 to produce simulated albedos of volcanic clouds at the TOMS wavelengths. It was found that the algorithm errors were about 5% for aerosol-free volcanic clouds; however, the errors grew to 30% when sulfate aerosols or volcanic ash was present in the clouds. In addition, the retrieval failed to produce credible values of ozone when sulfur dioxide was present.
- Model of volcanic clouds at ultraviolet wavelengths.
- Ash and aerosol produce a signature that is uniquely different from a pure Rayleigh atmosphere based on our radiative transfer studies of volcanic clouds. The optical model indicated we can extract information on the optical depth and index of refraction (type of ash) from the TOMS data if the inversion problems can be solved.
- Research on algorithm improvements to reduce the retrieval errors and to simultaneously retrieve sulfur dioxide, ozone, and two pieces of information about volcanic ash.
- The analysis of the Version 6 algorithm errors with simulated albedos led to the conclusion that the use of geometric path was the primary reason for the failure to produce valid sulfur dioxide and ozone retrievals. From space, the geometry of backscattering is far more complex than the direct path of sunlight to a ground observer. An effective path was defined from the model data which eliminated nearly all of the regrieval error in ozone and sulfur dioxide. In addition the modified retrievals produce correct values of the two aerosol parameters noted above. A new iterative retrieval algorithm for TOMS data which takes advantage of effective paths is under development.
- During this reporting period two new TOMS instruments were launched on the Earth Probe and ADEOS satellites. Our group has the primary responsibility to analyze and report volcanic eruptions detected by these satellites. Our primary dataset for initial evaluation of volcanic clouds is the Level 2 production data which generates sulfur dioxide and absorbing aerosol indexes (semi-quantitative measures). We have modified the production algorithm for wavelength changes in the new instruments.

- Operational needs exist in the aviation community for volcanic hazard data. In the past we have provided retrospective data to this community to confirm eruptions. We are supporting an effort by the FAA to provide TOMS data directly to the operational organizations. Earth Probe TOMS data are now collected in real-time by the FAA/NWS in Anchorage for ingestion in the air traffic control system. We are providing the software to process the data and guidance in use of the data.

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The Application of UV-Visible Radiative Transfer Modeling to *In Situ* Photochemical and Radiation Field Data from NASA's ASHOE/MAESA ER-2 Flight Campaign

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Research Objectives

Our research group at JHU/APL participated in the 1994 ASHOE/MAESA field campaign by providing photochemical rate coefficients (J-values) for photochemical reactions of interest in the upper troposphere and lower stratosphere along the flight tracks of the ER-2 aircraft. The use of J-values that are appropriate for the altitude, solar zenith angle and overhead ozone burden as observed from the ER-2 aircraft (rather than pre-computed values for standard scenarios such as the US Standard Atmosphere) provides a significant improvement in the agreement between observed species concentrations and simple photochemical models. Our presence in the field allowed us to generate these data in real-time for immediate analysis of the data. These J-values were subsequently used by a number of the ASHOE/MAESA science teams in the analysis of their data.

Summary of Progress and Results

We have been funded by UARP to 1) model the *in situ* spectroradiometer data from Environment Canada's Composition and Photodissociative Flux Measurement (CPFM) experiment flown during the SPADE, ASHOE/MAESA and STRAT campaigns, and to 2) analyze the effect of clouds and aerosols (both background sulfate and volcanic aerosols, such as those resulting from the 1991 eruption of Mt. Pinatubo) on the lower stratospheric/upper tropospheric radiation field, and in particular on the photodissociation rate coefficients associated with the CPFM experiment.

The largest uncertainty in the generation of photochemical J-values is the appropriateness of the input parameters. Three primary inputs are needed to constrain the model and generate J-values appropriate to the ER-2 flight track: 1) ozone profiles; 2) aerosol optical extinction profiles; and 3) effective ground albedos.

We have developed a number of collaborations begun during the ASHOE/MAESA campaign in order to obtain real-time data for input into the radiation field code. The use of METEOR-3 TOMS total ozone column data and *in situ* measurements of ozone profiles from balloon sondes flown from Lauder, New Zealand during the ASHOE/MAESA field campaign provided helped to constrain the uncertainty in the input ozone parameters used in the J-value calculations.

Our initial calculations of J-values have used seasonal aerosol optical extinction profiles from the MODTRAN database, scaled to match *in situ* ER-2 observations of aerosols. While aerosol optical extinction is not nearly as important during ASHOE/MAESA as during AASE-II or SPADE, when the Mt. Pinatubo aerosols were more abundant, small but significant decreases in important photolysis rates (especially J-NO_2) were calculated for south-bound flights on the second and third deployments when the solar zenith angles were quite large. The flight of 940601, with its crossing of the terminator, provided the rare opportunity to validate J-values for solar zenith angles greater than 90°.

The importance of changes in the apparent ground albedo, largely from high-altitude clouds, on the calculation of J-values became evident during ASHOE/MAESA. Our code now assimilates TOMS effective reflectance values (Pfister *et al.*) to simulate the changing albedo along the ER-2 flight track. We have also compared this formulation with "albedos" derived from the GMS satellite instrument (Pfister *et al.*) and the effective albedo at flight altitude as measured with the CPFM instrument aboard the ER-2 (McElroy *et al.*). The CPFM also allows us to analyze the wavelength-dependence of the effective albedo. The importance of changes in the apparent albedo along the flight track are most clearly seen in variations in the OH concentration, which often correlate well with albedo fluctuations and cloud events as monitored by the CPFM.

We are currently finishing an overhaul of our photochemical kinetic code which will not only make the calculations significantly faster, but will also facilitate the incorporation of *in situ* ER-2 data as inputs to the code. The original zero-dimensional photochemical model, used in the analysis of ER-2 ClO data has been augmented to model the photochemistry along the ER-2 flight track and along back-trajectories intersecting the flight track. Recent changes to the code will also facilitate easier comparison of the model results with ER-2 constituent and radiative datasets.

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Global Surface Ultraviolet Radiation Climatology from TOMS and ERBE Data

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Research Objectives

The objective of this project is to map the global distribution of biologically active surface ultraviolet radiation (UVR) using NASA satellite data in conjunction with detailed radiative transfer calculations. Global maps of total column ozone are provided by the Nimbus 7 Total Ozone Mapping Spectrometer (TOMS). Radiometrically calibrated observations of cloud cover and clear-sky planetary albedo are provided by the Earth Radiation Budget Experiment (ERBE). An efficient delta-Eddington radiative transfer model is used for surface UVR estimation, with spectral resolution throughout the UV-B (280-315 nanometers, nm) and UV-A (315 to 400 nm). The surface UVR calculations based on the satellite data will be validated using surface UVR-monitoring instruments deployed in the United States and Australia. The goal of this three-year project is to produce a global climatology of surface UVR flux between the latitudes 60°N and 60°S, for the period January 1985 to February 1990, when the TOMS and ERBE data overlap. Eventually this climatology will be archived on CD-ROM and will be made available for distribution to the scientific community.

Summary of Progress and Results

A method was developed to calculate the solar spectral ultraviolet irradiance (UVR) at the Earth's surface using NASA Total Ozone Mapping Spectrometer (TOMS), Earth Radiation Budget Experiment (ERBE) and International Satellite Cloud Climatology Project (ISCCP) data as input to radiative transfer models based on the delta-Eddington approximation. After co-location of the satellite data, the three step mapping procedure yields a spatial resolution (pixel size) of 2.5° x 2.5° (latitude x longitude). In the first step, the ERBE S-9 monthly/hourly clear-sky short-wave albedos are used to estimate the surface albedo, using a radiative transfer model that accounts for the Rayleigh scattering and trace gas absorption throughout the solar spectrum. In the second step, the short-wave radiation algorithm from the National Center for Atmospheric Research (NCAR) Community Climate Model (CCM2) is used to estimate an effective cloud optical depth from the ERBE S-9 monthly/hourly short-wave planetary albedos, along with the above surface albedo retrievals and the monthly averaged total column ozone abundances from TOMS. For both steps, total column water vapor abundance is taken from the ISCCP dataset, as measured by the Tiros Operational Vertical Sounder (TOVS) instrument aboard the NOAA polar orbiting satellites. Finally, with the above retrievals and ozone abundance from TOMS, a spectrally resolved delta-Eddington algorithm is used to estimate the monthly average local-noon UVR irradiance at the Earth's surface.

These modeled spectral irradiances were then weighted by several commonly used biological action spectra to yield dose rates.

This procedure for estimating surface UVR from satellite data is not the only one possible, but it has the advantage that each of the satellite measurements (ozone, cloud reflectance, and water vapor) was made by an orbiting instrument specifically designed to make the respective measurement. Having generated these surface UV-B maps, we then wished to investigate the effect of cloud variability on surface UV-B, in the context of global ozone depletion. To separate and contrast the effects of ozone and cloud cover, we repeated the delta-Eddington surface irradiance calculations for each month and year of ERBE cloud optical depth retrievals, but using only the TOMS ozone from 1985 for each respective month. This allowed us to estimate the variability in local noon UV-B that results only from interannual variability in cloud opacity. For each month, a sample standard deviation in the dose rate was computed for each pixel from this second set of delta-Eddington calculations.

We wished to determine, for a given month and location, the number of years for which we must steadily deplete the ozone layer before the resulting increase in UVR local noon dose rate becomes significant above the background variability due to interannual variability in cloud cover. To address this, we computed a baseline delta-Eddington UVR climatology using the 1985 TOMS ozone and the mean cloud effective optical depth from the five years of ERBE retrievals. Then in a computer simulation for each month and pixel, we allowed the 1985 TOMS ozone to be depleted (or in some cases increased) everywhere according to the trends reported by a study carried out by Professor John E. Frederick (University of Chicago). As the ozone was depleted in one year increments, the surface local-noon UVR dose rate was recomputed for each pixel. At each pixel, we noted the number of years that elapsed before the dose rate increased by a threshold of 1.96 sample standard deviations (that describe the interannual variability in UVR due to cloud cover). We find that throughout many temperate regions - including large parts of continental Europe, North and South America, New Zealand, Australia and southern Africa - interannual variability in cloud opacity is sufficiently small that by the end of this century, trends in summer average local-noon UVR dose rates relevant to mammalian skin cancer or plant damage should be significant with respect to cloud variability.

There are three remaining tasks for this project, which we expect to complete by April, 1997. First, we are conducting a study of the diurnal variation in surface UVR. This is made possible by the ERBE monthly/hourly data, which gives (monthly averaged) short-wave reflectance measurements for each daylight hour. Second, we are compiling some surface UV-B measurements made during 1985-1989 for comparison with the satellite-based climatology to provide some validation and suggest refinements as necessary. There are very few properly calibrated in situ UV-B measurements for this time period, but we have obtained datasets for 1989 from the Australian Radiation Laboratory (Melbourne and Brisbane), The Smithsonian Institution (Washington, DC area), and the National Science Foundation (Palmer Station, Antarctica). Third, we plan to complete the climatology for all daylight hours contained in the ERBE S-9 monthly/hourly dataset, and make the climatology available to the research community on CD-ROM.

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Theoretical Studies of Atmospheric Chemistry and Transport in the Stratosphere

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Research Objectives

The research addresses factors that regulate the composition of the stratosphere, particularly perturbations due to anthropogenic activity. We use a variety of radiative, photochemical, and dynamical models and detailed analyses of available data to define rates of transport in the stratosphere, to develop an improved understanding of the processes responsible for transport, and to analyze the effects of increased concentrations of trace gases.

Summary of Progress and Results

Metastable Phases in Polar Stratospheric Clouds (PSCs): A detailed study of thermodynamic data was undertaken to elucidate the phases of HNO_3, H_2O, and H_2SO_4 that can form in the polar stratosphere at temperatures below 205 K [Fox *et al.* 1995]. The analysis showed that a wide variety of metastable phases can form under stratospheric conditions, and that formation of metastable phases was strongly favored in the experimental conditions of an ultra-high vacuum system. The work showed that a particular mixed hydrate of all three species was especially favored in the initial nucleation process, converting to metastable $HNO_3 \bullet 2\ H_2O$. If such metastable phases form in the atmosphere, rapid accretion of mass will occur onto the first particles of the most stable phase ($HNO_3 \bullet 3\ H_2O$) to form or to be transported into a cloud of metastable particles, providing a potent mechanism for differential growth and sedimentation of particles containing HNO_3.

Distribution of Stratospheric H_2O: In the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE), the first high-resolution data were obtained for CO_2 simultaneously with data for H_2O. The minimum in H2O observed in fall near 19 km was shown by reference to the CO_2 data to represent the concentration during the previous January, when water reaches its seasonal minimum in the tropics. We conclude that the minimum in water vapor near 20 km, often called the "hygropause", is caused by the vertical propagation of the seasonal cycle for tropical H_2O and not by non-conservative processes such as overshooting cumulus clouds. This represents a change in paradigm for understanding stratospheric H_2O and for models of air movement between the stratosphere and troposphere.

2-D and 3-D Model Development and Applications: We have developed an interactive 2.5-D model of stratospheric dynamics, radiation and chemistry. The components of the model are: 1) a semispectral (gridpoints in latitude and altitude, Fourier components in longitude) primitive equation dynamics model which we can run in 2-D mode with externally specified Rossby wave mixing coefficients or in a 3-D mode with explicitly calculated planetary waves and internally derived 2-D transport parameters; 2) an accurate radiative heating scheme developed by Professor Guang-Yu Shi of the Institute for Atmospheric Physics of the Chinese Academy of Sciences; and 3) a newly developed family chemistry model. The model extends from the ground to 80 km with parameterized tropospheric heating rates.

Model Study of Transport Between Tropics and Mid-latitudes: Observations of long lived tracers (e.g., Upper Atmospheric Research Satellite (UARS) data for CH_4, HF and N_2O) show distinct latitudinal gradients in the subtropics indicating a barrier to mixing between the tropics and mid-latitudes of the stratosphere which has been conceptualized in the "tropical pipe model" described by [Plumb, 1996].

If there is a barrier to mixing in the subtropics, mass exchange between the tropics and the mid-latitudes of the stratosphere would be controlled by advection. Advective velocities are calculated in our model and the accuracy of the results can be tested by comparing model generated tropical and extratropical profiles of long lived tracers to observations. Our model produces a quantitative estimate of the flow through the "pipe walls" with a minimum of assumptions. It reproduces accurately the subtropical gradients in long lived tracers and is able to simulate observed CO_2/N_2O correlations. The speed of the residual mean circulation, its seasonal reversal, and the fact that extratropical mixing is strongest in winter combine to establish the observed seasonal behavior of CO_2 in the stratosphere.

Correlations between species with similar source characteristics such as CO_2 and N_2O were found to be insensitive to changes of K_{yy} within a large range once a threshold value necessary to distribute the signal throughout the hemisphere within a season is exceeded. The overturning rate can change by 30% as a function of the forcing in mid-latitudes without affecting the correlations. The change in the circulation pattern alters the N_2O and CO_2 distributions proportionally. Temperature changes induced by doubling/halving K_{yy} are of the order of 1 K, comparable to the uncertainty of the best available temperature measurements for the stratosphere [Eluszkiewicz, 1995].

The Effect of the Quasi Biennial Oscillation (QBO) on Tracers in Mid-Latitudes: The effect of the QBO on the mean meridional circulation consists in a modulation of the circulation in low latitudes which will result in variations in the mass flow across the tropical barrier. The 2-D model is being used to elucidate the effects of the QBO on the mass interchange between tropics and mid-latitudes and the associated influence on global ozone. We have introduced parameterized gravity wave momentum fluxes following Plumb [1987], and have obtained realistic QBO winds. Work is in progress to examine the effects of the QBO on tracers observed by UARS and on O_3.

Development of a 3-D Mechanistic Model: Only the largest scale planetary waves propagate to higher altitudes in the stratosphere and almost all the observed variability above 50 mb is associated with planetary wavenumbers one and two. This does not imply that it is sufficient to calculate just these waves. There is almost always a critical line present in the stratosphere and critical line interaction is the dominant process during a warming event. Studies using idealized models capable of very high resolution have shown that truncated models do not describe the critical line interaction accurately [Haynes and McIntyre, 1987]. It has been observed also in GCM type models that

simulations of nonlinear wave mean-flow interaction are sensitive to resolution [R. A. Plumb, personal communication].

We have run a series of tests to check the amount of cascading to smaller longitudinal scales needed to resolve a strong wave event. Runs were performed starting from the same initial condition and the same forcing for wavenumber one at the lower boundary (900 mb). The longitudinal truncation was varied between wavenumber 2 and wavenumber 12. Although the amplitudes of wave one do not differ markedly for different truncations, the maximum easterlies differ by more than a factor of 2. So does the rate of conversion of eddy potential energy to mean potential energy. Maximum energy conversion occurs roughly at the same time but is twice as strong for the case that includes only the first two wavenumbers. If more waves are allowed in the model, their amplitude is less than 1/10 that of wave one. Nevertheless, their presence is crucial during a nonlinear interaction.

We found that the evolution of the wave - mean flow interaction changes distinctly at four to six waves. Allowing more than six waves results in only minor changes in the maximum easterlies. This behavior is in agreement with findings of Haynes and McIntyre [1987]. Analysis of the behavior of potential vorticity and passive tracers for different truncations is in progress.

Minimal-Parameter 2D Model: We have constructed a minimal-parameter 2-D model based on the 3-pipe concept of Plumb [1995]. This concept presumes that, for the purposes of tracer transport, the stratosphere can be divided into 3 great domains, the tropics, northern mid-latitudes, and southern mid-latitudes, which can be treated as internally homogeneous. This idea is based on examination of ATMOS and ER-2 tracer data and on dynamical reasoning. Our model of this system adopted the mean diabatic circulation derived by Elusciewicz *et al.* [1995] from UARS/MLS data. We found that virtually all tracer distributions observed from satellites can be reproduced by this model without adjustable parameters. The seasonally-varying diabatic circulation provides almost all observed features of the global transport. This empirical approach facilitates the use of tracer measurements near the tropopause in a given year as a lower boundary specification and complements the 2-D and 3-D model work.

Publications

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The Analysis of Backscattered Ultraviolet Albedo Data to Infer Additional Information About the Atmosphere

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Research Objectives

The objective of this research is to obtain non-ozone-related information on the atmosphere from the SBUV instruments. The research concentrates on analysis of the spectral scan data, a special observation mode in the SBUV and SBUV/2 instruments in which the radiance backscattered from the atmosphere in the range 200 to 400 nm is measured in 0.2 nm steps. Previous work has shown that the intensity of nitric oxide gamma band emission can be derived from these data and used to infer the amount of NO in the upper stratosphere, mesosphere, and thermosphere. Strong SO_2 band structure near 300 nm can be used to uniquely identify the presence of SO_2 and measure it to an accuracy of n1 milli-atm-cm. The purpose of this research is to systematically analyze data from SBUV and NOAA 11 SBUV/2 to extend previous work on the distribution and long term changes in both nitric oxide and SO_2.

Summary of Progress and Results

Spectral scan data from the NOAA 11 SBUV/2 instrument were used to derive SO_2 for three days following the eruption of Mt. Pinatubo - 19 June, 1 July, and 17 July 1991. Band structure between 300 and 310 nm observed in the backscattered albedo uniquely identifies the presence of SO2 . Band ratios are used to infer SO_2 amounts to better accuracy (~10% to 20%) and sensitivity (about 0.5 milli-atm-cm of SO_2) than the TOMS retrieval, but with relatively poor spatial coverage because the measurement is nadir only. Seven scans showed detectable SO_2 on 19 June when the cloud was still very localized. On 1 July, there were 29 scans between 35°N and 12°S with SO_2, with the highest concentration detected over the Atlantic, and on 17 July, SO_2 was detected in 30 scans around the world, but in decreased concentration. Estimates of the total SO_2 budget made after the cloud had spread sufficiently for the sparse SBUV/2 sampling to be adequate indicated that there were 8.4 million metric tons (MMT) of SO_2 in the stratosphere on 1 July 1991, and 4.1 MMT remaining on 17 July which is consistent with an initial injection into the stratosphere of 12-15 MMT of SO_2.

Questions were raised by Schnetzler *et al.* [1995] about the accuracy of the SBUV-based SO_2 estimates because of inhomogeneity of the volcanic cloud. It was show by using the high density TOMS SO_2 dataset as an input "truth" dataset that, even with its poor coverage, the SBUV error due

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Interpretation of Remotely Sensed and *In Situ* Tropospheric CO Measurements

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Research Objectives

Comparison of existing space-based carbon monoxide (CO) column measurements to vertically resolved aircraft measurements will provide new insight into the application of these measurements. Specifically, the Measurement of Air Pollution from Satellites (MAPS) experiment retrieval algorithms will be applied to CO profile measurements made in the Global Tropospheric Experiment (GTE). The column CO retrievals from actual atmospheres will be evaluated for sensitivity to polluted layers, temperature structure, and interfering constituents seen in the actual profiles. The investigator will utilize data from GTE, and algorithms from MAPS.

Summary of Progress and Results

The investigator obtained and reviewed over 300 profiles from six GTE missions: CITE-3, TRACE-A, PEM WEST A, PEM WEST B, ABLE 3A, and ABLE 3B. In this process, we identified flights with sufficient data to proceed to analyze. Specifically we found flights which recorded data profiles from the surface up to near the tropopause, including concurrent measurements of the six most radiatively significant gases in the 4.67 μm band (CO, CO_2, CH_4, O_3, N_2O, and H_2O), plus vertically resolved temperature and pressure.

The GTE project measures water vapor, a key constituent, as dew point temperature. Converting this measurement into water vapor mixing ratio required the identification and merging of data and navigation files from the project archives and from the DAAC (temperature and total pressure). We performed these calculations and verified our results with the project. We selected flights from ABLE 2-A (1985) and TRACE-A (1992) for tropical atmospheres in austral spring, comparable to three of the four MAPS flights; from PEM WEST-A (September-October 1991) providing vast regions of background air; from CITE-3 for North American continental outflow; and from ABLE-3B for cold continental surfaces comparable to MAPS' April 1994 flight.

We developed a set of assumed values for the specified constituents for use when the measurements were absent. At altitudes above 12 km, the data are almost non-existent, and stratospheric profiles were constructed using models from Smith [1982] and the AFGL.

Forward radiative transfer calculations were performed on selected profiles to obtain spectrally resolved top-of-the-atmosphere radiances. The MAPS inversion algorithms, as developed by Neil

and Gormsen [1996], were applied to these "signals," resulting in retrieved CO and N_2O mixing ratios. Evaluation of these results is presently in progress.

This work was performed with ACMAP funding in FY 1996.

Publications

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Analysis of the Tropospheric Ozone Residual Method

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Research Objectives

The objective of this research is to examine the validity of the tropospheric ozone residual (TOR) method, which determines tropospheric column ozone by subtracting stratospheric column O_3 climatology, obtained from Stratospheric Aerosol and Gas Experiment (SAGE) or Solar Backscattered Ultraviolet Spectrometer (SBUV) stratospheric ozone column, from total column O_3 climatology, obtained from archived Total Ozone Mapping Spectrometer (TOMS) measurements.

Summary of Progress and Results

The validation of the TOR has been investigated by comparing TOR-derived tropospheric ozone climatology with ozonesonde-derived climatology [Fishman *et al.*, 1991]. Because ozonesonde measurements are sparse in time and space, a dataset with higher spatial and temporal resolution is required for estimating the error of TOR-derived climatology.

Based on the fact that the TOMS algorithm derives ozone column from the surface to the top of the atmosphere, Jiang and Yung [1996] (JY method) proposed a method for determining tropospheric ozone column in the lower troposphere by the difference between two locations with a topographic contrast (e.g., between the eastern Pacific Ocean and adjacent top of the Andes mountain ridge). From the analysis of the tropospheric ozone over the eastern Pacific Ocean derived from the JY method, the preliminary results of Kim and Newchurch [1996] indicate that the JY method is a capable tool to study tropospheric ozone climatology.

A climatology of lower tropospheric ozone over selected sites (e.g., adjacent to Andes, Kilimanjaro, New Guinea, and Madagascar) will be derived for the comparison with TOR-derived climatology. The error of the TOR-derived tropospheric ozone climatology will be estimated from this comparison.

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Publications

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Meteorological Measurements Support for Stratospheric Aircraft Missions

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Research Objectives

Obtain standard meteorological data for use by other investigators participating in NASA sponsored stratospheric aircraft missions. These data will be used for planning, forecasting, and post-mission analysis and interpretation of aircraft data.

Summary of Progress and Results

A UNIX-based workstation was obtained in FY 1991 (aeolus.gsfc.nasa.gov) for use on aircraft mission planning, forecasting, and post-mission analysis. This machine was originally used to provide in-field support for the Second Arctic Airborne Stratospheric Expedition (AASE II, 1991 through 1992), and the Stratospheric Photochemistry, Aerosols and Dynamics Experiment (SPADE, 1992 through 1993). Meteorological information such as the radiosondes and meteorological analyses have been used in much of the post-flight analyses by many of the aircraft groups, and these data have been placed on the CD-ROM's. This SGI workstation was upgraded in 1994 (notus.gsfc.nasa.gov) in order to be utilized for in-field support for the Airborne Southern Hemisphere Ozone Experiment (ASHOE) and the Measurements for Assessing the Effects of Stratospheric Aircraft (MAESA) missions during the course of 1994 in New Zealand. Since 1994, this machine has remained at GSFC, and continues to be utilized for supporting the Stratospheric Tracers of Atmospheric Transport (STRAT) and VOTE/TOTE experiments. Since this second machine is aging, we intend on upgrading to a more powerful machine. This upgraded machine will be utilized to support both the STRAT and POLARIS aircraft missions during 1996 and 1997.

Publications

None

Analysis of Stratospheric Aircraft Data, and Support for Aircraft Mission

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Research Objectives

The objective of this work was: 1) to use aircraft data to specifically improve our understanding of transport and mixing in the lower stratosphere; and 2) to provide a variety of meteorological products to the science teams involved with aircraft field campaigns (including gridded meteorological data, conventional met observations such as radiosondes, parcel back trajectories, high resolution gravity wave model forecasts, and cooling rates estimated from a radiative transfer model).

Summary of Progress and Results

The GSFC group actively supported the ASHOE/MAESA experiment in 1994, and the STRAT experiment during 1995 through 1996.

The poleward transport of tropical air in the lower stratosphere during AASE II was examined using contour advection calculations. These calculations showed that filaments of tropical air extended into mid-latitudes, and wrapped around the equatorward edge of the polar jet. Simultaneously filaments are drawn from the polar vortex and are intermingled with the filaments of tropical air. The tropical filaments were consistent with measurements of chemical tracers taken aboard the ER-2 and DC-8 aircraft which show localized regions, in mid-latitudes, of air with the characteristics of tropical air [Waugh *et al.*, 1994a].

In addition to poleward transport, we also worked on analyzing intrusions of mid-latitude air into the polar vortex in January and February 1992 during AASE II. Direct confirmation of the presence of the intrusions and of their calculated locations was provided by aerosol observations from the airborne differential absorption laser lidar aboard the NASA DC-8, and from *in situ* measurements

from the NASA ER-2. These types of events were found to be relatively infrequent [Plumb *et al.*, 1994].

Ejection of material from the polar vortex during AASE II was also investigated using contour advection with surgery. These calculations show that Rossby wave breaking is an ongoing occurrence during these periods and that air is ejected from the polar vortex in the form of long filamentary structures. There is good qualitative agreement between these filaments and measurements of chemical tracers taken aboard the NASA ER-2 aircraft. This process transfers vortex air into mid-latitudes and also produces a narrow region of fine-scale filaments surrounding the polar vortex. Among other things, this makes it difficult to define a vortex edge [Waugh *et al.*, 1994b].

A global mountain wave model was used to examine small-scale disturbances encountered by the NASA high-altitude ER-2 during AASE II. The magnitude and location of observed large wave events were well reproduced, and a correlation was found between patches of moderate turbulence encountered by the ER-2 and locations of predicted breaking mountain waves [Bacmeister *et al.*, 1994].

Horizontal spectra of various quantities was investigated using 73 ER-2 flights. Velocity and potential temperature spectra in the 100 to 1-km wavelength range were found to deviate significantly from the uniform -5/3 power law. Instead, steeper spectra consistent with a -3 power law are observed at scales smaller than 3 km. Shallower spectra are observed at scales longer than 6 km. These observed velocity and potential temperature spectra were consistent with gravity waves. Ozone and N_2O spectra in the 100 to 1-km wavelength range exhibit a -5/3 power law. This may reflect interactions between gravity waves and filamentary structures in the trace gas field produced by enstrophy-cascading two-dimensional turbulence [Bacmeister *et al.*, 1996].

Data obtained during the NASA Stratosphere Troposphere Exchange Project (STEP) Mid-Latitude Field Experiment showed laminae of ozone, water, and condensation nuclei in the stratosphere in association with a mid-latitude stratosphere-troposphere folding event. These quasi-horizontal laminae have been interpreted as evidence of ultra-low frequency gravity waves. We found that these laminae more probably resulted from differential advection, rather than transport by ultra-low frequency gravity waves [Newman and Schoeberl, 1995].

Publications

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Evaluation of Climate Forcing by Upper Tropospheric Aerosol Particles Using Observations from SAGE II

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Research Objectives

Retrieved profiles of aerosol extinction coefficient obtained with the Stratospheric Aerosol and Gas Experiment II (SAGE II) instrument frequently extend below the tropopause, suggesting the possibility of using this sensor to monitor the upper tropospheric aerosol. By combining SAGE II profiles of aerosol extinction coefficient with satellite- and ground-based observations of total aerosol optical depth, the contribution of the upper tropospheric aerosol to the direct radiative forcing of climate by aerosol particles can be determined. The objectives of the project were to:

- Evaluate the consistency of vertical profiles of aerosol light extinction from SAGE II with observations of aerosol light scattering and optical depth at NOAA's baseline observatory at Mauna Loa, Hawaii, and with observations of the vertical distribution of aerosol size distribution obtained by the University of Wyoming.
- Evaluate the relative contributions from the lower troposphere, upper troposphere, and stratosphere to aerosol optical depth over the global oceans using satellite observations.

Summary of Progress and Results

We combined the SAGE II extinction profiles with NOAA's operational product of total aerosol optical depth (AOD) derived from the Advanced Very High Resolution Radiometer (AVHRR) to determine the contributions of lower tropospheric (below 6 km altitude), upper tropospheric, and stratospheric aerosols to the total aerosol optical depth. This analysis was performed for the eight seasons prior to the eruption of Mt. Pinatubo in June 1991, representing volcanically unperturbed conditions, and for nine different regions over the global oceans. In most cases, the combined optical thickness of the upper troposphere and stratosphere, interpolated from SAGE II observations at 525 and 1020 nm to the AVHRR wavelength of 630 nm, was less then 0.01, with comparable contributions from the upper troposphere and stratosphere, and only a small fraction of the total optical depth determined with AVHRR. The exceptions corresponded to cases when the total optical depth was very low (winter over the Southern Ocean, North Pacific Ocean, and North Atlantic

Ocean). We conclude that, during volcanically-unperturbed periods, the direct aerosol radiative forcing is dominated by aerosols in the lower troposphere.

Publications

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Construction of a Long-Term Climatology of Antarctic Polar Stratospheric Clouds by an Automated Classification System Using AVHRR and UARS Data

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Research Objectives

Polar stratospheric clouds (PSCs) play an important role in the ozone depletion process over the polar regions as they provide surfaces upon which heterogeneous reactions occur that ultimately lead to the destruction of ozone. Present methods of PSC detection by solar occultation satellites and lidar offer limited spatial and temporal information, particularly in the region of the polar night, and do not allow for the assemblage of a long-term climatology of PSCs. Thus, questions remain as to the timing of the onset and duration of PSCs, as well as to their geographic extent. Advanced Very High Resolution Radiometer (AVHRR) sensors onboard the National Oceanic and Atmospheric Administration (NOAA) polar orbiting satellites have been collecting data over the polar regions since 1979, and provide excellent temporal and spatial coverage of both polar regions. We are investigating the use of AVHRR thermal infrared data to detect PSCs over Antarctica. PSC detection algorithms based on AVHRR data are being verified with Upper Atmosphere Research Satellite (UARS) Cryogenic Limb Array Etalon Spectrometer (CLAES) stratospheric temperature and aerosol extinction coefficient data, as well as National Meteorological Center (NMC) radiosonde data and Antarctic Automatic Weather Station (AWS) surface temperature data. The results obtained from this study will be incorporated into an automated rule-based classification system for PSC detection which can be applied to the entire record of AVHRR data in order to assemble a long-term climatology.

Summary of Progress and Results

Initially, our research focused on the detection of optically thick PSCs in the AVHRR over West Antarctica. This is the region where the majority of PSCs form, and where surface temperatures are relatively warmer, thus providing good thermal contrast between PSCs and the surface. We determined that thick PSCs can be detected in the AVHRR channel 5 (12 μm) imagery using density-slicing techniques (color contouring of temperatures). We are producing thick PSC analysis maps that show the percent coverage of AVHRR pixels at or below 188 K, 195 K, and 200 K (temperatures that encompass brightness temperatures of both opaque and semi-transparent PSCs).

While density-slicing methods work well for thick PSCs, other methods are needed to detect thinner PSCs, as they are not readily discriminated in the density-sliced thermal imagery due to the transmission of upwelling radiation from below that contaminates the PSC signature. We have begun the task of developing methods for the detection of optically thin PSCs in AVHRR imagery collected over the Weddell Sea region of West Antarctica. Supervised methods, such as multispectral and neural network classification, require a high quality verification dataset that is both temporally and spatially coincident with the AVHRR imagery. Based on the observed rapid movement and/or dissipation of optically thick PSCs, we are using only those CLAES data points that were collected within 20 minutes of an AVHRR pass. Approximately three percent of the CLAES data collected over the Weddell Sea region match this restricted time interval.

Multispectral color-composite infrared imagery has proven useful in visual/manual analysis of optically thin cirrus in nighttime AVHRR imagery when channels 3, 4, and 5 are assigned to the red, green, and blue guns respectively. Thin cirrus appears bluish, and lower clouds and surfaces appear pinkish. When Antarctic AVHRR data are displayed in similar color composites, PSCs appear to have a distinct spectral response, with thick PSCs appearing white, and thin PSCs exhibiting a distinctive blue color.

The AVHRR channel 4-5 difference image has been shown to be useful in identifying thin cirrus and contrails in AVHRR imagery in both tropical and polar regions. This difference image is also useful in PSC detection, as it show the thin PSC in white tones and as distinct from thick PSC, tropospheric cloud and surface ice which display darker tones. In addition, various texture measures, such as range, have been tested and are useful in separating thin PSCs from other clouds and surface features.

Based on the above results, we believe that thin PSCs have a spectral signature in the AVHRR data even when present over cold backgrounds. This signature is verified by feature-space analyses of the images. When training set data (samples of various subjects selected from visual interpretation of the AVHRR color-composite imagery and derived channels and from CLAES verification data) for AVHRR channels 4-5 vs. channel 5 are plotted, there is good separability of PSC from other classes such as tropospheric cloud and ice surface.

We have used the various multispectral information to classify several AVHRR images using two methods: 1) a Euclidean minimum distance classifier; and 2) a back-propagation neural network. Our initial results show that the neural network appears to better classify thin PSCs. In the neural network classification, the thin PSC shape is more cloud-like and is more clearly drawn, and there is also less confusion between tropospheric cloud and stratospheric cloud.

The results of using multispectral techniques in the detection of thin PSCs are very encouraging. However, some significant hurdles remain. We have identified areas that need more work: namely, the production of better verification datasets and the further development and testing of more sophisticated PSC detection algorithms. We intend to incorporate the use other datasets, such as HIRS/2 cloud top pressure retrievals, and SAM II and lidar measurements to improve and expand our verification dataset. In the next year, we plan to refine our feature-space analysis and complete the multispectral and neural network classification testing. Our goal is to create a final algorithm or series of algorithms that are universal with respect to seasonal and annual variations in temperature and aerosol amounts. Finally, we will apply these algorithms to a small sample of Arctic imagery to determine if PSCs can be identified in AVHRR imagery over the Arctic region.

Publications

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Meteorological Studies for Airborne Mission

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Research Objectives

The objectives of this task are twofold. First, we provide meteorological guidance on tropospheric weather to the airborne missions for NASA's Upper Atmosphere Research Program. This includes providing in real time, and archiving, extensive satellite meteorological datasets for use by the mission scientist and by the science team.

Second, we are addressing the issue of the lower stratospheric water budget with a view toward answering the following questions: (1) How is air, and water, transferred into the lower tropical stratosphere from the troposphere? and (2) how much, and by what mechanism, is air transferred into the lowest part of the mid-latitude stratosphere, and how can water measurements constrain the type of mechanisms?. These issues are important, since water vapor has a major effect on stratospheric chemistry. In particular, any attempt to calculate climatic changes in stratospheric water using models must include the essence of the mechanisms that transfer the water upward.

Summary of Progress and Results

We have provided the Airborne Southern Hemisphere Ozone Experiment/Measurements for the Atmospheric Effects of Stratospheric Aircraft (ASHOE/MAESA) science team with a comprehensive satellite dataset along the flight track of the ER-2, including TOMS total ozone and UV reflectivity data, as well as visible reflectivities and IR brightness temperatures from geostationary meteorological satellites. This information is needed to calculate photodissociation along the flight track. Thus, it is an essential cog in the complex scheme the science team uses to establish the degree to which we understand stratospheric photochemistry.

We are also engaged in the analysis of ASHOE/MAESA data in two areas. First, we are using aircraft tracer data, meteorological analyses, and meteorological satellite data to look at tropical-mid-latitude exchange in the lower stratosphere. Preliminary results showing the penetration of mid-latitude air into the tropics were presented at the IUGG meeting in Boulder, CO. Second, we are trying to evaluate the overall level of turbulence in the Southern Hemisphere stratosphere. This is important for: (1) the dissipation of chemically disturbed streamers from the Antarctic vortex as they move towards mid-latitudes; and (2) the upward propagation of waves generated in the troposphere.

So far, we have shown that the vortex region has very little turbulence compared to other regions of the stratosphere. Preliminary results were presented at the ASHOE/MAESA science team meeting in April 1995.

For the Stratospheric Tracers of Atmospheric Transport (STRAT) project, we are engaged in ongoing development of analysis tools for meteorological satellite data. In particular, we have devoted attention to the 6 to 7 micron "water vapor" channel (WVC) available on geostationary satellites. Radiance at these wavelengths is related to upper tropospheric (500 to 200 mb) water vapor. Since the stratosphere is dry, and since the tropopause often descends below 200 mb in mid-latitudes, output from this channel is often a qualitative indicator of tropopause height. Indeed, the relationship between 350 K (near the tropopause in mid-latitudes) potential vorticity and WVC radiance is clear, both from previous work, and from the animation loops of superimposed PV and WVC we have done for the STRAT May 1995 deployment. An example of the use of this imagery for the STRAT dataset was presented at the SPARC (Stratospheric Processes and their Results for Climate) workshop on stratosphere-troposphere exchange near Montreal Quebec in early June 1995.

More recently, we have performed the following tasks for aircraft mission meteorological guidance. We have developed some simple cloud height algorithms that can be used in real time for flight planning for the low altitude (tropospheric) ER-2 flights. These use a combination of meteorological analyses and satellite imagery to determine the cloud altitude at any point in a satellite image. We have also set up a web site to communicate our data to the science team—http://telsci.arc.nasa.gov.

On the science side, more recent work includes back trajectory analyses of STRAT data that shows that cloud and radiosonde data can be used to constrain the mechanisms that move water into the mid-latitude lower stratosphere.

We have also supported the Tropical Ozone Transport Experiment and the Vortex Ozone Transport Experiment (TOTE and VOTE). These show sheets of subvisible cirrus in the tropics south of Hawaii. Our analysis, using our meteorological satellite data, meteorological fields from the GSFC Assimilation model, and trajectory analysis tools from GSFC, suggests that subvisible cirrus observed near the tropopause south of Hawaii originates from convective outflows at the tropical tropopause level in the western Pacific, flows northward, evaporates as it descends and warms, travels eastward with the subtropical jet at 25-30N, and recondenses as the flow turns southward at Hawaiian longitudes. This theory is a result of collaboration with other members of the science team.

Publications

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Large-Scale Stratospheric Transport Processes

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Research Objectives

This project aims at the elucidation and quantification of stratospheric transport processes through (i) investigations of isentropic transport using model and contour advection studies; (ii) investigations of 3-D transport using observations and a 3-D trajectory model; and (iii) the construction of a conceptual, global theory of stratospheric tracer transport. In (i), the main focus is on the lower stratosphere and the tropics. In (ii), the main focuses are an understanding of the distribution of "age" in the stratosphere and on 3-D transport in the polar vortices.

Summary of Progress and Results

(i) *Isentropic transport:* Analysis of data from the AASE2, SPADE, and ASHOE experiments has continued, in conjunction with contour advection analyses of stratospheric transport. Amongst other things, this has revealed, through anomalous tracer interrelationships, the mixing of polar and mid-latitude air during vortex breakdown in spring 1995 (during SPADE). The absence of such anomalies in mid-winter mid-latitude data (from AASE2 and ASHOE) is indicative of the weakness of transport out of the deep vortex during winter. We have also analyzed transport between tropics and middle latitudes, using contour advection. Winds from routine global analyses were used to demonstrate tropics-to-mid-latitude transport events, but attempts to analyze transport into the tropics were inconclusive, as winds from different meteorological centers produced very different results. Analysis of low-latitude transport in the "SKYHI" GCM is in progress. We have also recently begun a series of experiments with a 3-D global model to investigate transport and dynamics in the polar lower stratosphere, especially the structure of the polar vortex in this region.

(ii) *3-D trajectory studies:* Using a 3-D trajectory code, in which particles are advected by 3-D winds from the SKYHI GCM, we have illustrated the formation of vortex and subtropical tracer edges by surf-zone mixing. We have also compiled age statistics for this model; although the stratospheric ages are rather older than observations suggest, the distribution of the statistics (still being analyzed) gives a concise picture of model transport.

(iii) *Conceptual theory of stratospheric transport:* An earlier global picture of stratospheric as a single, rapidly interacting system has been revised into a "tropical pipe" model, which incorporates total or partial isolation of the tropical stratosphere from mid-latitude air. A numerical model based on this picture reproduces observed species correlations rather well.

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SAGE II Aerosol Studies

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Research Objectives

The objectives of this research are to: (1) use principal component analysis to study the information content and particle size sensitivity of multi-wavelength SAGE II aerosol measurements; (2) develop optimal techniques for retrieving aerosol physical properties such as total surface area and total mass; and (3) use the retrieved parameters to define global and polar aerosol and cloud climatologies.

Summary of Progress and Results

Two significant climatological studies of stratospheric aerosols using SAGE data have been completed in the past year. The first study compares stratospheric aerosol loading measured by SAGE in 1979 and by SAGE II in 1989 through 1991 [Thomason *et al.*, 1996a], periods that are often termed background (non-volcanic) periods because aerosol levels were lower then than at any other times in the modern measurement era. Results show that depending on latitude, the 1-μm aerosol optical depth in 1989 through 1991 was 10% to 30% higher than that observed in 1979. SAGE II data demonstrate that the latter period (prior to the June 1991 eruption of Mt. Pinatubo) was characterized by an ongoing global recovery from the eruptions of El Chichon in 1982 and Nevada del Ruiz in 1985, with a further complication introduced by the February 1990 Kelut eruption. The slow decrease of aerosol loading in mid-northern latitudes in 1989 and 1990 is most likely the combined result of the continuing loss of aerosol from the stratosphere following these volcanic injections, variations in the transport of aerosol from the tropical reservoir associated with the phase of the quasi-biennial oscillation, and possibly the influence of small volcanic events during 1990. Therefore, the increase in aerosol loading between 1979 and 1989 through 1991 cannot be completely attributed to anthropogenic sources such as aircraft sulfur, as has been suggested.

The second study [Thomason *et al.*, 1996b] presents a global climatology of stratospheric aerosol surface area density derived using the multi-wavelength aerosol extinction measurements from SAGE II for the period 1984 through 1994. This climatology significantly contributes to our ability to parameterize aerosol-catalyzed heterogeneous chemical processes that lead to ozone destruction and involve both natural aerosol and human-produced reactive chlorine [Solomon *et al.*, 1996; Portmann *et al.*, 1996]. The spatial and temporal variability of aerosol surface area density at 15.5, 20.5, and 25.5 km are presented as well as cumulative statistical distributions (median, 10 to

percentile, and 1-percentile) as a function of altitude and latitude. The time period encompasses the injection and dissipation of the aerosol associated with the June 1991 Mount Pinatubo eruption as well as the low loading period of 1989 through 1991. During this period, aerosol surface area density varied by more than a factor 30 at some altitudes. Surface area densities derived from SAGE II and from the University of Wyoming optical particle counters are compared for 1991 through 1994 and are shown to be in generally good agreement, though some differences were noted. An extended climatology derived using single wavelength aerosol measurements by the Stratospheric Aerosol Measurement (SAM) II (1978 through 1994) and SAGE (1979 through 1981) instruments is also included.

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Statistical Analysis of Atmospheric Temperature and Ozone Data for Trend Features and Comparisons with Model Calculations

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Research Objectives

The principal purpose of this research is to perform statistical analyses of worldwide temperature profile data and atmospheric total ozone and ozone profile data for the detection of trend. Our research efforts have been concentrated primarily in the following areas:

- Time series analysis of ground-based Dobson and satellite total ozone mapping spectrometer (TOMS) total ozone data to investigate ozone trends over different seasons and regions, and solar cycle effects on ozone;
- Analysis of the effects of stratospheric aerosols on ground-based Umkehr ozone profile measurements and trend analysis of aerosol-corrected Umkehr data, and of Umkehr data obtained using a new inversion algorithm;
- Comparison of stratospheric ozone trends by examination of ozonesonde and Umkehr data;
- Comparison of stratospheric ozone trends and solar cycle effects using Umkehr and combined solar backscattered ultraviolet (SBUV), SBUV/2 satellite data;
- Trend analysis of ground-based rawinsonde station and satellite microwave sounding unit-channel 4 (MSU-4) lower stratospheric temperature data and comparisons with model calculations.

Summary of Progress and Results

Seasonal Trend Analysis of Ground-Based and TOMS Satellite Total Ozone Data: A seasonal trend analysis of published Dobson (including stations' newly revised and Brewer-simulated Dobson) total ozone data through 1991 from a network of 56 stations has been performed, using three different data periods. The seasonal trend model considered allows for a different trend for each month of the year to examine the seasonal nature of ozone trend behavior, and also includes an F10.7 cm solar flux term and a 50 mb equatorial wind QBO term. Random effects models for the individual station seasonal trend estimates, to allow for station and regional variations, are used to combine individual estimates to obtain overall trend estimates for different seasons of the year as a

function of latitude. The trend results for the longest data period 1964 through 1991 indicate substantial negative trends in ozone in the higher northern latitudes during the winter and spring seasons, of the order of -2.5% per decade, some evidence of negative trend in the higher southern latitudes (30°S-55°S) during all seasons, and trends close to zero for all seasons over the 30°S-30°N latitude range.

For the shortest data period, November 1978 through 1991, there is an indication that trends have become more negative in the higher northern latitudes, especially during the winter and spring seasons, and also in the higher southern latitudes in all seasons. A seasonal trend analysis of zonal averages of total ozone mapping spectrometer (TOMS) satellite total ozone data for the comparable period November 1978 through 1991 has also been performed, and moderately good agreement is found between trends in Dobson and TOMS data over this period. These results are described in detail in Reinsel *et al.* [1994b].

Comparison of Trend Analyses for Umkehr Data Using New and Previous Inversion Algorithms: Ozone vertical profile Umkehr data for layers 3 to 9 (~15 to 49 km in altitude) from 12 stations, using both previous and new inversion algorithms, have been analyzed for trends. The trends estimated for the Umkehr data from the two algorithms were compared using two data periods, 1968 through 1991 and 1977 through 1991. Both non-seasonal and seasonal trend models were fitted, using statistical models that also included F10.7 cm solar flux and stratospheric optical thickness terms to account for solar cycle variations in ozone and errors in the Umkehr measurements caused by stratospheric aerosols from volcanic activity. The overall annual trends in Umkehr data are found to be significantly negative, of the order of -5% per decade, for layers 7 and 8 using both inversion algorithms. The largest negative trends occur in these layers under the new algorithm, whereas in the previous algorithm the most negative trend occurs in layer 9. The trend estimates, both annual and seasonal, are substantially different between the two algorithms for layers 3, 4, and 9, where trends from the new algorithm data are about 2% per decade less negative, with less appreciable differences in layers 7 and 8. The trend results from the two data periods are similar, except for layer 3 where trends become more negative, by about -2% per decade, for 1977 through 1991. More details concerning trend results of this analysis are given in Reinsel *et al.* [1994a].

Comparison of Stratospheric Ozone Trends By Examination of Umkehr and Ozonesonde Data: The non-seasonal and seasonal trend behavior of ozone profile data has been examined using both ozonesonde and Umkehr measurements in a consistent manner, covering the time period of 1968 through 1991. This provides a useful overall comparison of trend results between the two data sources. In this trend analysis study, ozone profile data from 10 ozonesonde stations and 11 Umkehr stations, all located in the mid-latitudes of the Northern Hemisphere (about 30°N to 55°N), were considered. Our trend results obtained reaffirm the finding of significant negative ozone trends in both the lower stratosphere (15 to 20 km), of about -6% per decade, and upper stratosphere (35 to 50 km), of about -6% per decade, separated by a nodal point of little or no trend in the region of 25 to 30 km altitude. The upper stratosphere decrease is, apparently, associated with the classic gas phase chemical effect of the chlorofluorocarbons, whereas the cause of the lower stratospheric decline is still under investigation, but may be associated with the chlorine and bromine chemistry in this altitude region. A detailed description of the analysis and results is presented in Miller *et al.* [1995].

Comparison of Stratospheric Ozone Trends and Solar Effects Using Umkehr and Combined SBUV, SBUV/2 Satellite Data: The stratospheric ozone trends and responses to the 11-year solar cycle

(represented by the F10.7 cm radio flux) are estimated from both ground-based Umkehr records and the combined Nimbus 7 SBUV and NOAA 11 SBUV/2 satellite records, and the results from the two datasets are compared. The analysis considers ozone data for the northern mid-latitudes (30°N-50°N) at altitudes between 25 and 45 km for the period 1977 through June 1991. In particular, the effects of spatial sampling differences between the two datasets on the estimated trend and solar signals is investigated. The trends estimated from the two ozone datasets are nearly identical at all altitude levels except 35 km, where the Umkehr data indicate a somewhat more negative trend. The trend is approximately zero near 25 km, but becomes more negative in the upper stratosphere, reaching nearly -7% per decade in the 40 to 45 km region. The upper stratospheric decreases are consistent with chemical model results and are associated with the gas phase chemical effect of CFC and other ozone-destroying chemicals. The ozone correlations with the F10.7 cm solar flux are similar in the two ozone datasets, with statistically significant in-phase solar-induced ozone variations above 30 km. Estimates of the solar cycle effect on ozone at 40 to 45 km altitude obtained from a regression-time series model indicate solar-induced variations in ozone of about 4.5% from solar cycle minimum to maximum. Analysis of the satellite overpass data at the Umkehr station locations shows that the average trend of the ground-based data from the 11 Umkehr stations is a good approximation for the trend in the 30°N-50°N zonal mean satellite series. The results of this analysis are presented in detail in Miller *et al.* [1996].

Trend Analysis of Lower Stratospheric Rawinsonde and MSU-4 Temperature Data: A preliminary trend analysis of the lower stratospheric temperature data from the microwave sounding unit (MSU) channel 4 satellite source for the period 1979 through 1992 has been initiated, and comparison of these temperature data and their trend behavior with corresponding data and trends constructed from available rawinsonde station temperature data for the same time period is considered. Rawinsonde temperature data recorded at 10 pressure levels from about 225 stations were used and a vertically-weighted average temperature series was constructed from each station's data, using weights over the different pressure levels that are consistent with the MSU channel 4 temperature data weighting function. Some basic comparisons of the rawinsonde-based temperature data with collocated MSU channel 4 data have been performed, and substantial differences in trend behaviors have been noticed in certain cases. The differences in behavior between rawinsonde-based and MSU-4 temperature data seem to be similar among many of the rawinsonde stations within a given geographical/political region, but the patterns of disagreement between rawinsonde and MSU-4 data are not consistent among the different regions. Further study and analysis of these data are needed.

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A Reprocessing of the Nimbus 7 LIMS Dataset

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Research Objectives

This effort is aimed at generating an improved version of the Nimbus 7 LIMS dataset that is compatible with those from UARS. The HITRAN 92 line parameters are to be used for the reprocessing.

Summary of Progress and Results

A number of studies have been performed to determine the improvements that one can expect from a reprocessed LIMS dataset. Both the forward radiance and retrieval models have been updated, and new emissivity tables have been generated for the primary and interfering species in each of the LIMS channels. Almost all of the known biases in the archived version of the LIMS data are being corrected in this version. The new data will be available at greater vertical and horizontal resolution. The operational processing should be underway in autumn of 1996 and the data should be available for general use in 1997.

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Analysis of Atmospheric Spectra for Trace Gases

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Research Objectives

The objective of this work is the comprehensive analysis of high-resolution atmospheric spectra recorded in the mid-Infrared (IR) to obtain simultaneous measurements of concentration profiles and total columns of important atmospheric trace gases. Solar absorption spectra recorded with ground-based and balloon-borne interferometers at remote sites are used in the analysis. Emphasis is the determination of long-term trends and seasonal cycles of molecules involved in O_3 chemistry.

Summary of Progress and Results

High-resolution (up to 0.002 cm^{-1} HWHM) Network for the Detection of Stratospheric Change (NDSC) solar spectra recorded at Mauna Loa (Hawaii), Jungfraujoch (Switzerland), and Lauder (New Zealand) have been analyzed to determine trends in the abundances of a number of important atmospheric gases, in collaboration with the NDSC co-investigators from these stations. Molecules studied during the last three years include $ClONO_2$, HCN, C_2H_6, O_3, and HNO_3. The work has been supplemented with analyses atmospheric measurements obtained from the National Solar Observatory on Kitt Peak, Arizona, and studies to improve spectroscopic parameters needed for such atmospheric studies.

Measurements from the Jungfraujoch show a regular long-term increase in the $ClONO_2$ column with occasional factor two to three enhancements during the mid-winter to early spring [Rinsland *et al.*, 1996a]. The high $ClONO_2$ columns indicate the occasional presence of chemically-processed air above the station. This is corroborated by trajectories calculated for the stratospheric airmasses sounded on these occasions. Excluding data from this time of the year, the ISSJ database reflects a linear rate of increase and 1-sigma uncertainty equal to $(4.0 \pm 0.7)\%$ yr^{-1} referenced to 1990.0.

About 200 infrared solar spectra recorded at 0.01-cm^{-1} resolution on 71 days between November 1991 and July 1993 at the Mauna Loa NDSC station have been analyzed to study temporal variations in the total column of atmospheric ethane (C_2H_6) above the site [Rinsland *et al.*, 1994a]. The results

were derived from the analysis of the unresolved n_7 band $^PQ_3$ subbranch at 2976.8 cm^{-1}. A distinct seasonal cycle is observed with a factor of 2 variation, a maximum total column of 1.16 x 10^{16} molecules cm^{-2} at the end of winter, and a minimum total column of 0.53 x 10^{16} molecules cm^{-2} at the end of summer. Our measurements are compared with previous observations and model predictions.

The phase and relative amplitude of the seasonal cycle of the C_2H_6 total column above the Lauder NDSC station are similar to corresponding values determined from infrared measurements at the Jungfraujoch and Mauna Loa NDSC stations, but the inferred absolute magnitudes of the Lauder surface level mixing ratios during the same season are significantly lower [Rinsland *et al,* 1994b]. The Lauder C_2H_6 measurements have been compared with published Southern Hemisphere surface level sampling measurements and two-dimensional model calculations.

A program (SFIT) developed as part of this effort is widely used for NDSC IR retrievals. An improved program (SFIT2) based on the Rodgers optimum estimation method has been used to retrieve O_3 profile information in 3 layers (ground-12 km, 12-20 km, and 20-100 km) [Pougatchev et al., 1995b]. Results comparing profile retrievals from Lauder spectra and correlative Dobson, ozonesonde, and microwave measurements agree within a few percent [Pougatchev *et al.,* 1996]. Infrared-to-Dobson total column ratios derived from different infrared bands ranged from 0.96 to 1.02 with the lower wavenumber bands generally yielding the lower ratios [Rinsland *et al.,* 1996b]. The results do not support the revised O_3 intensity scale currently used to process O_3 infrared measurements from 2 instruments on the Upper Atmosphere Research Satellite.

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Photochemical Modeling of Field Data

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Research Objectives

Our research objective is to analyze of measurements of radicals, reservoir gases, long-lived tracers of atmospheric transport, and aerosol surface area obtained from the ER-2 during ER-2 field campaigns to examine our understanding of the photochemical and dynamical processes that regulate O_3 in the lower stratosphere and upper troposphere.

Summary of Progress and Results

Analysis of ER-2 data obtained during SPADE showed that reactions involving hydrogen radicals are the most important ozone removal process in the lower stratosphere, followed by reactions involving chlorine radicals. Reactions involving nitrogen radicals were found to be least important of the three families of radicals, consistent with theoretical predictions of models that allow for heterogeneous hydrolysis of N_2O_5.

Generally good agreement was found between theory and observed concentrations of hydrogen, nitrogen, and chlorine radicals during SPADE. Our theoretical estimates relied on a photochemical steady state model constrained by measured values of radical precursors (i.e., O_3, NO_y, Cl_y inferred from CFCs, H_2O, CH_4, CO), surface area, ozone column, and albedo. Observed concentrations of OH and HO_2 tended to be systematically higher than theory by 10 to 15%, and displayed a rapid increase in concentration at sunrise that has since been attributed to photolysis of HOBr produced by the heterogeneous hydrolysis of $BrNO_3$. Theory and observation tended to agree to within 15% for ClO and the sum $NO+NO_2$, but the NO/NO_2 ratio was observed to be about 35% higher than predicted. The most notable disagreement between theory and observation was for HCl, which was about half the predicted value for much of SPADE. However, analysis of simultaneous observations of ClO, NO, NO_2, and O_3 suggested good agreement between daytime ClO and predicted $ClNO_3$, suggesting the "missing chlorine" was not residing in the form of $ClNO_3$. Observations obtained in the lowermost stratosphere just above the tropopause revealed layers approximately 0.5 km thick of near zero levels of NO, and enhanced levels of ClO (ClO = 25% of Cly) for air that was cold (T = 205 K), wet (H_2O = 20 ppm), and had fairly high surface area (5 um^2/cm^3). These observations provide the first evidence for cold evidence for the occurrence of rapid heterogeneous involving $ClNO_3$ on cold sulfate aerosol for non-polar air.

Our analysis of long-lived tracers measured during ASHOE/MAESA revealed rates of exchange of tropical and mid-latitude air in the lower stratosphere are slower than had been thought, and comparable to the time for ascent in the tropical upwelling region. These results offer a possible explanation for why many 2D models currently underestimate the long-term decline in O_3 due to CFCs, and demonstrate that exhaust from a future fleet of SSTs will be transported to the mid-stratosphere. We found generally good agreement between theory and observation of the NO/NO_y and NO/NO_2 ratios over a wide range of latitudes during ASHOE/MAESA, in contrast to the SPADE observations for NO/NO_2. Good agreement was found between $ClNO_3$ inferred from ER-2 measurements of ClO, NO, and O_3 and ATMOS measurements of $ClNO_3$, for air masses observed at similar times and locations.

Our preliminary analysis of tropospheric measurements of hydrogen and nitrogen radicals obtained during ASHOE/MAESA reveal good agreement between theory and observation of NO/NO_y throughout the upper troposphere, in contrast to published analyses of DC-8 data, and the presence of nearly a factor of 2 or more OH than calculated based solely on production of HO_x from H_2O and CH_4. Continued analyses of ASHOE/MAESA and STRAT data, especially tropospheric measurements of hydrogen and nitrogen radicals, is the subject of ongoing research.

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Model Interpretation of Aircraft, Balloon, and Shuttle Data

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Research Objectives

Our research objective is to analyze measurements obtained from aircraft (ER-2 and DC-8), balloon-borne (MkIV, BLISS, SLS, and FIRS), shuttle (ATMOS, MAS, CHRISTA/MAHRSI) and satellite platforms (SAGE II, HALOE, MLS) to examine the chemical, dynamical, and thermodynamic processes that regulate the abundance of stratospheric and tropospheric ozone.

Summary of Progress and Results

Examination of measurements by ATMOS in the Arctic and Antarctic polar vortices has revealed similar descent rates and the existence of air of mesospheric origin in both regions during winter. Strong horizontal gradients along the vortex edge were evidence for significant barriers to mixing until at least mid-April in the Arctic during 1993 and mid-November for the Antarctic during 1994. A layer of denitrified air extending higher in altitude than the region of dehydration was observed in the Antarctic vortex. This layer was observed below a region of "re-nitrification", apparently related to mesospheric production of NO_y. ATMOS and MAS measurements at tropical and middle latitudes revealed evidence for the existence of a channel for production of HCl from some process other than $Cl+CH_4$ and $Cl+HO_2$. ATMOS profiles of H_2O+2CH_4 were consistent with a maximum in the profile of H_2 near 50 km altitude, consistent with theory, and showed evidence for a seasonal variation in the abundance of H_2O entering the stratosphere.

ATMOS measurements in 1985 and 1994 revealed no change in the stratospheric abundance of OCS, the dominant source of aerosols for the background (i.e., non-volcanic) stratosphere, suggesting that if, as has been suggested, there is an anthropogenic component to production of OCS, it has not changed in strength during the past decade. Similar trends and, surprisingly, similar stratospheric lifetimes were observed for SF_6 and $CHClF_2$. A comparison of ATMOS and ER-2 measurements for air masses observed at similar times and geographic locations showed excellent agreement for tracers of atmospheric transport (i.e., N_2O, CH_4, CFCs, H_2O), except CO, which tends to be about 40% higher from ATMOS than from the ALIAS instrument on the ER-2.

Analysis of measurements of HO_x, NO_x, and ClO_x compounds from the FIRS-2 and SLS balloon-borne instruments revealed generally good agreement between theory and observation, except levels of reactive chlorine tend to be 50% lower than predicted near 40 km altitude. A model allowing for production of HCl from either $ClO+OH$ or $ClO+HO_2$ was shown to results in better agreement with the observations. Measurements of NO, NO_y, O_3, and aerosol from another set of balloon

instruments showed good agreement with the predicted dependence of NO/NO_y on aerosol surface area.

Analysis of high resolution solar absorption spectra revealed an upper limit of 0.5 pptv for the stratospheric abundance of inorganic iodine, which together with recent laboratory measurements for the rate of IO+ClO, indicates iodine chemistry can not be responsible for the trends in lower stratospheric ozone observed during the past several decades.

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Meteorological Analysis for STRAT

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Research Objectives

This investigation's objective is to support the STRAT (Stratospheric Tracers of Atmospheric Transport) experiment in three principal ways:

- First, meteorological data are provided to the field site, consisting of radiosonde observations and 3-D gridded analyses and forecasts from the Goddard Data Assimilation Office (DAO).
- Second, flight planning software enhances the mission scientists' ability to direct the aircraft flight track to areas yielding the highest scientific benefit, and a gravity wave model provides forecasts of severe turbulence over areas which can then be avoided.
- Third, chemical and trajectory modeling studies are used to aid in interpreting the data collected by STRAT.

Summary of Progress and Results

This investigation has been active in the four STRAT deployments staged thus far: May 1995, October-November 1995, January-February 1996, and July-August 1996. Because the scientific value returned by any given STRAT flight is heavily dependent on the meteorological situation, it is advantageous to have current meteorological data and forecasts available in the field. Therefore, twice daily during the deployments, all of the required radiosonde reports, gridded analyses, and forecasts are pulled from computers at GSFC to the field site. (Software was written for STRAT to perform this data transfer persistently across even poor network connections at remote sites.) The data are plotted into a series of maps and cross-sectional plots which are used to determine the current status and likely evolution of the dynamical situation in the stratosphere and upper troposphere.

Also twice per day during the California STRAT deployments, the gravity wave model is run to forecast areas of strong turbulence. During the January-February deployment, these forecasts indicated that severe turbulence from breaking gravity waves was likely over Northern California, and the flight tracks were relocated out off the California coast.

STRAT relies on "stacked" flights (flights going back and forth between two waypoints at six or seven discrete altitudes) to obtain vertical cross-sections of tropospheric and middle-world air. Because such flights require careful planning in choosing length, location, and orientation, the flight planner software, used by GSFC personnel in previous experiments, has been extensively modified for STRAT, with new features added to facilitate planning stacked flights. Forecast temperature profiles are examined with the most recent radiosonde data to determine the likely positions of the tropopause and the middle world.

After each flight, the appropriate meteorological analyses along the flight track are made available to the experimenters. The Microwave Temperature Profiler team, for example, has made use of these data in their final data reduction. Also, high-resolution maps and cross-sections of potential vorticity are made using the Reverse Domain Filling (RDF) method; these aid in interpreting the origin of air associated with features seen in the experimental data.

The STRAT upper tropospheric dataset (~10-13 km), thanks to direct measurements of OH and HO2, provides the first test of photochemical theory in the upper troposphere with ER-2 *in situ* measurements. An instantaneous photochemical steady-state "point model" (Thompson *et al.*, 1996) is used in this investigation to assimilate a merged set of 30-second averaged ER-2 data.

The first set of model runs uses a chemical scheme that includes 81 reactions and photodissociations, and 28 species are solved for, including byproducts of methane and ethane oxidation. With O_3/CO/NO/temp/H_2O/HC fixed from the ER-2 measurements, OH and HO_2 are computed.

STRAT data have been simulated for four flights: 26 October 1995, 7 November 1995, 2 February 1996, and 8 February 1996. A summary of results to date is:

- Calculated OH and HO_2 are lower than observed (by a factor of 2 or greater) but the OH/HO_2 ratio is in good agreement for the standard run in all cases. NO_y calculated and observed are in good agreement in all but one case.
- Constraining the model with measured OH and J's improves the agreement with HO_2 but adding HO_x enhances equilibrium amounts of PAN, HNO_4, HNO_3 so that NO_y(computed) > NO_y (observed) by 1.3-1.5.
- Adding acetone moderates but does not eliminate the OH disagreement. PAN increases and NO_y becomes greater than observed.

In addition to this chemical modeling, comparisons are underway to assess the degree to which the DAO model accurately forecasts the height of the tropopause, as well how well contours of Ertel's potential vorticity reflect the tropopause position.

Publications

None

Radiative and Chemical Effects of Clouds and Aerosols

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Summary of Progress and Results

An important aspect of atmospheric chemistry models is the computation of photolysis rates. These rates must be computed accurately because sunlight leading to photodissociation is the primary driver of atmospheric chemistry both in the stratosphere and troposphere. It is also important that these rates be computed efficiently so that models can be used to examine a variety of situations deemed to be of interest. It is particularly important that the interaction with aerosols and clouds be computed accurately because their impact on the radiation field and therefore on photolysis is significant. To accomplish this goal we constructed a two-stream model that was deployed and tested both in the solar and the infrared part of the spectrum. Thus, it can be used to compute both solar heating rates and infrared cooling rates as well as photolysis rates. This code was tested thoroughly both for clear and cloudy conditions, and under cloud-free skies with aerosols. The results show that the efficient two-stream approximation can be used for the computation of photolysis rates without significant loss in accuracy both under clear an cloudy conditions. Thus, the 2-stream approach yields results that are typically accurate to within the combined uncertainties of cross sections and quantum yields used in photochemical models [Kylling *et al.*, 1995].

This brings up another important issue. As more accurate cross sections becomes available it is important to be able to incorporate those in the radiative transfer code without a major effort. In practice such an upgrade of cross sections and quantum yields in models for calculation of photodissociation rates is often a very tedious task. To facilitate this task we have developed a separate tool for easy upgrading of cross sections and quantum yields. This tool considerably eases and speeds up upgrading of cross section and quantum yields.

To test the capabilities of our codes we have participated in the Photolysis Rate Intercomparison for Assessment Models, motivated by the Assessment Model Workshop in November 1993 held at Boulder, CO, and summarized in *The Atmospheric Effects of Stratospheric Aircraft: A Fourth Program Report,* NASA Reference Publication 1359, R. S. Stolarski and H. L. Wesoky, Editors, 1995. Our model was found to agree well with those of other participants. We would like to see more comprehensive tests carried out for cloudy and aerosol-loaded atmospheres.

Two particular codes have been developed and made available to the research community as a result of this project. These are a general purpose code for computation of UV/visible spectral radiation. One of these code, named UVSPEC, can be used by researchers for analysis of measurement data

[see e.g., Zeng *et al.*, 1994; Mayer *et al.*, 1996] or as a component of another model [Zeng *et al.*, 1996]. It can be used to compute spectra of UV/visible radiation (intensities and fluxes) at any desired level in the atmosphere. Another code, called PHODIS, is specifically designed for the computation of photolysis rates, and is therefore intended to be used as a subroutine in a photochemical model. Both of these codes can compute the radiation field in a vertically inhomogenous atmosphere very accurately using a multi-stream discrete-ordinate code [DISORT, Stamnes *et al.*, 1998] or approximately using the two-stream code mentioned above [Kylling *et al.*, 1995].

For application to high latitudes and twilight situations in general, it is important to have codes that work properly in spherical geometry. We have developed such codes and made them available to interested users in the atmospheric chemistry community. It is also important to realize that UV and visible radiation depend strongly on surface albedo for clear as well as aerosol-loaded and cloudy atmospheres. The UV albedo of snow may be as high as 94-97% [Blumthaler and Ambach, 1988; Grenfell and Warren, 1994]. Under cloudy conditions, multiple reflections between the snow-covered surface and the atmosphere may lead to considerable increase in UV exposure. The contribution from the surface to the downward irradiance depends on the spherical albedo, which is the same as the flux reflectance for uniform illumination of the atmosphere from below [Stamnes, 1982]. For a cloudy atmosphere this spherical albedo is large and gives rise to a nonlinear behavior of the downward irradiance as a function of surface albedo [Kylling *et al.*, 1995]. This yields a much more pronounced dependence on surface albedo for cloudy than for clear atmospheric conditions.

To test the performance of the photolysis codes we have collaborated with Dr. Ivar Isaksen's group at the University of Oslo. Our photolysis codes have been incorporated into Isaksen's chemistry models, and runs have been made with their old photodissociation program and with our model. Results have been analyzed and reasonable agreement was found for clear atmospheres. Our code for computing photodissociation rates is currently used in their two- and three-dimensional tropospheric chemistry models.

The spherical version of our UVSPEC program for calculation of radiative quantities in the UV and visible regions of the spectrum, has been extended to calculate off-zenith irradiances. It is being used by experimentalists to investigate the possibility for measuring NO_2 profiles from ground-based experiments by looking in off-zenith directions. We have also participated in an intercomparison of radiation codes used to calculate air masses for large solar zenith angles [Slusser *et al.*, 1995].

Our UVSPEC and PHODIS programs developed with support from this project are currently being used by a number of different research groups around the world. The need for such codes has made us spend a considerable amount of time porting our radiative transfer models to various computers and helping researchers use them. Part of this work has involved writing User's Guides for our programs. This has benefited the research community as a whole by avoiding needless duplications of computer program development.

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Analysis of Stratospheric Trace-Gas Satellite Measurements

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Research Objectives

The stratospheric trace-gas constituents methane and nitrous oxide are important greenhouse gases and links in the chain leading to ozone depletion. Moreover, as long-lived tracers of stratospheric circulation, knowledge of their distribution and transport provides critical assessment of global stratospheric circulation models. Stratospheric and Mesospheric Sounder (SAMS) methane and nitrous oxide constituent measurements were taken a decade prior to the Upper Atmosphere Research Satellite (UARS) observations and provide unique, historical data series for these gases involved in greenhouse and ozone-depletion effects. The objectives of this grant are to determine the three-dimensional and temporal variability of satellite-derived global measurements of methane and nitrous oxide from three years of SAMS data fields, and to use these in dynamical calculations to determine the circulation in the stratosphere and lower mesosphere.

Summary of Progress and Results

Stratospheric circulation dynamics have been investigated using three years of zonal mean SAMS nitrous oxide and methane data fields. Pulses of constituent concentration are observed to exhibit seasonal upwelling and latitudinal propagation from low latitudes towards the poles. Both "effective transport" and Transformed Eulerian Mean formulations were used. The former employed a novel calculational technique to derive both the zonal mean transport velocity components as well as the eddy diffusion tensor as a function of time, height, and latitude.

We also investigated zonal asymmetries (planetary scale waves) in SAMS constituent data. Our results indicate that with careful data preprocessing and analysis it is possible to isolate large waves in SAMS stratospheric constituents. Zonal wave one (one wavelength fits around a latitude circle) perturbations with periods of a few weeks in the upper stratosphere are investigated in Ziemke and Stanford [1995]. The paper assesses the strengths and weaknesses of analyzing wave-like features in SAMS, including model simulation of aliasing due to the irregular sampling inherent in the data.

Publications

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Interpretation of Ozone Trends (Reanalysis of Nimbus 4 BUV Data)

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Research Objectives

Satellite data has yielded important information on trends in stratospheric ozone. This task has supported research into the nature of these trends including statistical trend analyses of the TOMS and SBUV time series. A new direction now being taken is the reanalysis of the Nimbus 4 BUV instrument record from 1970 through 1977. An analysis of the springtime Antarctic ozone over this period shows many similarities to what was observed by the Nimbus 7 TOMS in 1979. Extension of the satellite trends back to 1970 using BUV data will require an intercalibration with the Nimbus 7 instruments across the data gap. This will likely be done using coincidences with Dobson ground stations. Examination of the statistical model assumptions has been started, in particular the question of using a surrogate for the time variation of stratospheric aerosol content [Solomon *et al., JGR, 101,* 6713, 1996]. Determination of the best surrogate will be aided by a study of our monte carlo uncertainty analysis which is now being applied to the decadal trend from chlorine problem by David Considine. His model results will be fitted to solar cycle and aerosol surrogates to determine the degree of their separability in the record. Various forms of aerosol surrogate will be used such as extinction or extinction times chlorine concentration. These studies are expected to yield a higher degree of confidence in our understanding of what trends have occurred and should help significantly in detecting and interpreting the expected turnaround in the ozone amount over the next decade or so.

Summary of Progress and Results

This task has evolved over a number of years from a primarily model-based study to a data-based study. The modeling work included a cooperative study with a number of other researchers of the springtime recovery of reservoir concentrations in and near the Arctic and Antarctic polar vortices [Douglass *et al.,* 1995]. It has also included the development of a monte carlo uncertainty propagation scheme applied to the Goddard 2D stratospheric photochemistry model. Some preliminary results were included in the recent assessment report of the Atmospheric Effects of Stratospheric Aircraft program (AESA, Stolarski *et al.,* 1995). The same uncertainty propagation model using uncertainties in reaction rate coefficients, photolysis cross sections, and heterogeneous reaction probabilities is now being applied to the decadal evolution of ozone with changing chlorine by David Considine (this is a cooperative effort with separate funding for Considine). Both studies

will be presented at the Quadrennial Ozone Symposium [Stolarski *et al.*, 1996a; Considine *et al.*, 1996].

As part of this task data from the BUV instrument on the Nimbus 4 satellite has been used to construct maps of the measured total ozone field over the Antarctic region during the Austral springs of 1970 through 1975. The October monthly mean map of total ozone for the early 1970s shows a circumpolar maximum ring which has peak values of greater than 500 DU and a shallow polar minimum with total ozone column amounts of about 300 DU. This picture is similar to that observed in 1979 by the Nimbus 7 TOMS instrument. It is in agreement with the measurements made by the ground-based Dobson instruments at Halley Bay and Syowa during the early 1970s thus demonstrating that the lack of an "ozone hole" in those measurements is not because of the location of the measurements. There is no evidence to indicate that the stratospheric temperatures during the early 1970s were unusually warm. In fact, 1979 appears to be an unusually warm year which may mask the beginnings of the significant chemical depletion in the first year's TOMS data. The data from the BUV instrument further confirm the conclusion drawn from the Halley Bay data record that there is no evidence for a solar cycle modulation of the depth of the springtime minimum in Antarctic ozone. These results are given in a paper which is in preparation [Stolarski *et al.*, 1996b].

These results for the Antarctic region are not dependent on the details of the calibration of the instrument because the differences of interest are large. In order to extend the study to the examination of long-term trends on a global scale, the calibration must be considered in more detail. The next step is to evaluate the BUV measurements with respect to the Dobson ground-based network. The first step in preparation for this has been the careful reevaluation of the comparison of the Nimbus 7 TOMS instrument with the ground based record. This has been recently redone (partially funded by this task) by Labow and McPeters [1995]. The calculation of total ozone from balloonsondes and their use in comparison to BUV-type instruments has also been examined [partially funded by this task, see McPeters *et al.*, 1996].

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Flight Planning and Constituent Modeling for the STRAT Campaign Using the GEOS-1 Data Assimilation System

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Research Objectives

The primary purpose of this investigation is to provide meteorological forecasts and analyses in support of flight planning during STRAT deployments.

The second part of this investigation involves 3-D constituent modeling using an off-line chemistry and transport model. The constituent modeling has two applications to STRAT. First, model-generated constituent simulations will be used in support of mission planning, i.e., predicting constituent mixing ratios and correlations at various latitudes and seasons. The second application is to use constituent modeling to quantify transport and provide a continuous, 3-D context for the interpretation and analysis of aircraft data, which are by nature spatially and temporally limited. At the same time, aircraft data provide a means to verify model transport.

Summary of Progress and Results

Support of flight planning: This investigation has provided forecasts and analyses to project scientists for flight planning during all STRAT deployments to date (May 1995 to August 1996). The quality of both the forecast and assimilated products is high as judged by 1) agreement with MMS temperatures and winds, and 2) the ability of the forecasts to reliably predict the existence and location of phenomena of interest, such as vortex filaments. In the mean, no biases in winds or temperatures are seen between the assimilation products and the MMS measurements. Wind forecasts and analyses in the tropics agree less closely with MMS than in the extratropics.

Support of mission planning: A one-year 3-D simulation of N_2O, F-11, and CO_2 produced with winds from the NCAR CCM2 (courtesy of Doug Rotman, LLNL) has been used to assist in mission planning for the 1996 aircraft and balloon (OMS) deployments. At the 1995 STRAT Science Meeting, this simulation was used to address specific issues, such as what kind of variability can be expected from these tracers at different latitudes and seasons, how well can that variability be sampled by just a few aircraft or balloon flights, how would the observations be changed by the timing of the deployments, and what kind of sampling strategies are suggested by the simulation.

Transport studies: The propagation of the phase and amplitude of the tropospheric CO_2 seasonal cycle to the tropics and to the global lower stratosphere (LS) provides a signature of the path of transport. ER-2 CO_2 observations, including those from STRAT, have been made over a 46-month period and they allow the construction of CO_2 time series at many latitudes and altitudes. By comparing the phase and amplitude of observed CO_2 time series with model simulations, we can evaluate model transport in the upper troposphere (UT), ascent rates in the tropical LS, and transport rates in the lowermost stratosphere. In 1996, additional constituent simulations were performed (courtesy of Doug Rotman, LLNL) using winds from the GSFC GEOS-1. Some results of the comparison of NCAR and GSFC CO2 simulations with ER-2 data are presented below.

In the Northern Hemisphere (NH) mid-latitudes, observations show a 6-7 ppmv seasonal cycle in the UT (May maximum) which is damped out near the tropopause. This suggests strong stratospheric influence at the tropopause, a sensible result as there must be net downward flux at the mid-latitude tropopause. In the LS (~430 K), a weak seasonal cycle with a November maximum is seen. This maximum is the attenuated tropospheric maximum from the previous spring, transported to the LS via the tropical tropopause. In the subtropics, a seasonal cycle (~3 ppmv) with a May maximum is seen at the tropopause, suggesting a stronger tropospheric influence at the subtropical tropopause. This signal is damped out just above the tropopause (~400 K), but at 420-450 K a 6-month phase-lagged signal (i.e., November maximum) appears, just as in the mid-latitudes. The tropical tropopause appears to have a roughly 3 ppmv signal with a May maximum, which propagates into the LS and attenuates with altitude.

Boering *et al.* [*Science,* submitted] conclude that the spring maximum arrives at the tropical tropopause (~375 K) in May and ascends to 420-430 K by October/November, where it quickly is transported out to the NH mid-latitudes.

While the NCAR and GSFC models do a reasonable job of simulating the seasonal cycle in the NH upper troposphere, this cycle appears to simply diffuse upward, creating a LS signal which arrives in August. The observations show a damping of the seasonal cycle near the mid-latitude tropopause, but the models' cycles do not, suggesting that the models' LS cycle may not have arrived via the tropical LS. Further suggestion of a transport problem is given by the models' tropical profiles which don't compare well with the observations. Neither model shows a bulge at 430 K in the October profile corresponding to the ascent of the NH spring maximum. Without this large amplitude signal (~3 ppmv) available for mixing out to the extratropics, it will be difficult for the models to correctly reproduce the observed seasonal cycle in the lower stratosphere.

Publications

None

Tropical Tropospheric Ozone from TOMS: Variability and Related Process Studies

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Research Objectives

There are two objectives to this research: (1) To develop, with Co-Is at University of Maryland and with the Ozone Processing Team, more accurate products for the retrieval of tropospheric ozone column in the tropics; and (2) to interpret variations in the tropical tropospheric ozone field on daily, seasonal and annual scales. For the latter, trajectory and photochemical models are used. Global modeling related to tropical ozone formation, especially the effect of deep convection, is also performed, to aid in interpreting tropical ozone distributions.

Summary of Progress and Results

In terms of improving tropospheric ozone products from TOMS, the cloud corrections initiated under the previous three years, were applied to TOMS data more extensively. Cloud and efficiency corrections were applied to a case study in 1989 in which the TOMS-SAGE difference method was used to derive tropospheric ozone [Hudson *et al.*, 1996]. ISCCP-derived cloud heights were used in v. 7 TOMS [Hsu *et al.*, JGR, 1996]. A particular focus of tropical ozone retrievals was the period covered by the SAFARI/TRACE-A field missions of September-October 1992; TRACE-A (Transport and Atmospheric Chemistry near the Equator - Atlantic) was a GTE field campaign in Brazil, southern Africa and Ascension Island. Kim *et al.* [1996] describes a mew method for deriving the tropical tropospheric ozone field which agrees very well with the DC-8 UV-DIAL ozone measurements and with ozonesondes launched over Africa and Brazil [Diab *et al*, 1996] during the field mission. The ozone column depths are consistent with photochemical rates of ozone formation and with trajectories over the south Atlantic Basin [Thompson *et al.*, 1996a-c]. Trajectories are being used to interpret the new smoke and aerosol products from TOMS [Hsu *et al.*, *GRL*, 1996]. Other analyses of tropical ozone are examining the wave-like structure that shows as higher total

ozone over the Atlantic than the Pacific [Ziemke *et al.*, 1996]. Transport studies relevant to deep convective influences on tropical ozone are described by Allen *et al.*, [1996a, b] and by Lelieveld *et al.* [1996].

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DC-8 Mission Planning

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Research Objectives

In conjunction with Mark Schoeberl of Goddard, we completed the Tropical Ozone Transport Experiment and the Vortex Ozone Transport Experiment (TOTE/VOTE) during December 1995 through February 1996. The organization and completion of the SUbsonic aircraft Contrail and Cloud Effects Special Study (SUCCESS) was done during April and May 1996.

Summary of Progress and Results

The TOTE/VOTE missions were designed to investigate the transport of CH_4, H_2O and aerosols between dynamically different parts of the stratosphere. The NASA DC-8 aircraft was used to carry Raman and Differential Absorption Lidar (DIAL) lidars, as well as supporting equipment, from the North Polar regions to the tropics. The mission investigated the predictability of transport across the edge of the polar winter vortex and transport between the tropics and mid-latitude. In addition, subvisibile cirrus clouds near the troposphere were observed, possibly carrying material from the upper troposphere into the stratosphere. The first mission science meeting was held in June 1996. During the rest of the year, data analysis and paper preparation will be done.

The SUCCESS mission was designed to better understand the radiative properties of cirrus clouds, and to search for any possible effects of aircraft on such clouds. The NASA ER-2 was used as a surrogate satellite to investigate the radiative properties of cirrus and of contrails; the NASA DC-8 as a cloud microphysics and chemistry *in situ* measurements platform; the NASA T-39 to study the exhaust from other aircraft; and a NASA 757 to generate contrails and exhaust. The SUCCESS observations primarily occurred over the DOE's Atmospheric Radiation Measurements site in Northern Oklahoma. A number of new microphysical and chemical instruments were flown successfully during this 6-week field campaign.

Publications

Mission documents for the TOTE/VOTE and SUCCESS flight series.

Theoretical Investigations of Stratospheric Particulates

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Research Objectives

We have investigated the formation mechanisms of various types of polar stratospheric clouds (PSCs). Our work points to the presence of multiple types of PSC particles forming under different conditions including the formation mechanisms for new particles in the polar night, and the evolution of volcanic aerosols. In addition, we investigated the role of subvisible cirrus clouds in limiting the transport of water into the stratosphere.

Summary of Progress and Results

We have studied the physical and chemical properties of polar stratospheric clouds with the goal of improving our ability to predict their occurrence and their properties that might be relevant for heterogeneous chemistry. We find that liquid ternary solution particles form if the stratospheric air is warmer than about 210 K, so that preexisting sulfate particles would have melted. On the other hand, air that is kept at temperatures below about 195 K tends to have solid PSC particles in it. Lidar observations of these various types of clouds reveal that solid and liquid particles are sometimes mixed together in the same region. In addition, there appear to be more than one kind of solid particle. From the point of view of lidar observations, these two solids are distinguished by their typical particle size. We have worked to obtain the optical properties of materials that may compose PSCs so that observations of their spectra, or light scattering behavior can better determine the properties of the clouds and have shown that downward moving air in the winter polar regions can lead to the formation of new particles as sunlight converts SO_2 from high altitude into sulfuric acid. We investigated the ways in which volcanic clouds evolve in the stratosphere and have shown that radiative heating of the clouds, due to absorption of upwelling infrared energy from the earth, plays a significant role in the subsequent transport of the material. Finally, we have studied how cirrus clouds form near the tropical tropopause and whether the formation of such clouds is an important regulator of the water vapor that enters the stratosphere.

Publications

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Stratospheric Heterogeneous Chemistry and Microphysics: Model Development, Validation and Applications

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Research Objectives

The objectives of this project were to define the chemical and physical processes leading to stratospheric ozone change that involve polar stratospheric clouds (PSCs) and the reactions occurring on the surfaces of PSC particles; to study the formation processes, and the physical and chemical properties of PSCs, that are relevant to atmospheric chemistry and to the interpretation of field measurements taken during polar stratosphere missions; to develop quantitative models describing PSC microphysics and heterogeneous chemical processes; to assimilate laboratory and field data into these models; to calculate the extent of chemical processing on PSCs and the impact of specific microphysical processes on polar composition and ozone depletion.

Summary of Progress and Results

During the course of the project, a new coupled microphysics/physical-chemistry/ photochemistry model for stratospheric sulfate aerosols and nitric acid and ice PSCs was developed and applied to analyze data collected during NASA's Second Airborne Arctic Stratospheric Expedition (AASE-II) and other missions [Drdla *et al.*, 1992, 1993; Drdla, 1996]. In this model, detailed treatments of multi-component sulfate aerosol physical chemistry (see below), sulfate aerosol microphysics, polar stratospheric cloud microphysics, PSC ice surface chemistry [Tabazadeh and Turco, 1993a], as well as homogeneous gas-phase chemistry were included for the first time. In recent studies focusing on AASE measurements, the PSC model was used to analyze specific measurements from an aircraft deployment of an aerosol impactor, FSSP, and NO_y detector [Drdla, 1996; Drdla *et al.*, 1994]. The calculated results are in excellent agreement with observations for particle volumes as well as NO_y concentrations, thus confirming the importance of supercooled sulfate/nitrate droplets in PSC formation. The same model has been applied to perform a statistical study of PSC properties in the Northern Hemisphere using several hundred high-latitude air parcel trajectories obtained from Goddard. The rates of ozone depletion along trajectories with different meteorological histories are presently being systematically evaluated to identify the principal relationships between ozone loss and aerosol state.

Under this project, we formulated a detailed quantitative model that predicts the multi-component composition of sulfate aerosols under stratospheric conditions, including sulfuric, nitric, hydrochloric, hydrofluoric and hydrobromic acids [Tabazadeh *et al.*, 1994a, b]. This work defined for the first time the behavior of liquid ternary-system type-1b PSCs. The model also allows the

compositions and reactivities of sulfate aerosols to be calculated over the entire range of environmental conditions encountered in the stratosphere (and has been incorporated into a trajectory/microphysics model-see above). Important conclusions that derived from this work over the last few years include the following: the HNO_3 content of liquid-state aerosols dominate PSCs below about 195 K; the freezing of nitric acid ice from sulfate aerosol solutions is likely to occur within a few degrees K of the water vapor frost point; the uptake and reactions of HCl in liquid aerosols is a critical component of PSC heterogeneous chemistry [Turco and Hamill, 1982; Drdla, 1996]. In a related application of this work, the inefficiency of chlorine injection into the stratosphere during major volcanic eruptions was explained on the basis of nucleation of sulfuric acid aerosols in rising volcanic plumes leading to the formation of supercooled water droplets on these aerosols, which efficiently scavenges HCl via precipitation [Tabazadeh and Turco, 1993b].

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Mapping Antarctic Ozone in the 1970s from Visible-Channel Data

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Research Objectives

Accurate, detailed maps of total ozone were not available until the launch of the Total Ozone Mapping Spectrometer (TOMS) in late 1978. However, the Scanning Radiometer (SR), on board the NOAA satellites during the 1970s, included a visible channel that overlapped closely with the Chappuis absorption band of ozone around 600 nm. The Antarctic atmosphere and surface contain no other significant absorbers of radiation at that wavelength. We are investigating whether SR data can be used to map Antarctic ozone prior to 1978.

Summary of Progress and Results

We have developed a method, using a simple calculation of two-way transmittance, to obtain total ozone from data taken by the AVHRR during the 1980s. We compare our derived ozone amounts with those of TOMS Version 7. Our method works only over scenes whose albedos are large and unvarying (snow and cloud-covered snow). We have incorporated the following processes in our model.

- An anisotropic reflectance function for the snow-cloud system, obtained by minimizing the difference between TOMS-derived ozone and AVHRR-derived ozone for certain years in the 1980s.
- Rejection of anomalously bright or dark scenes, interpreted to be cloud edges.
- Accounting for the change in brightness caused by large-scale surface slope, which is important even for slopes of less than half a degree if the sun is low.
- Accounting for spherical-earth effects, in particular the fact that the solar zenith angle at the ozone layer differs significantly from that at the satellite's surface target, when the sun is low.
- Incorporation of the new measurements of Chappuis-band absorption coefficients for ozone.
- An accurate band-transmission function for the ozone absorption band.
- A weighting scheme to favor ozone retrievals made at angles where the anisotropic reflectance factor is more reliably known (near-nadir viewing).
- Choice of a space scale (200 km) and a time scale (5 days) for averaging of derived ozone amounts.

We are continuing to work on improvements to the method and estimation of its accuracy. This includes estimation of the drift of the satellite
sensors.

Publications

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Stratospheric Tracers of Atmospheric Transport (STRAT) Project Scientist

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Research Objectives

The objectives of the STRAT mission (1995-96) are to define global rates of transport in the stratosphere using extensive measurements of stratospheric tracer distributions obtained using NASA's ER-2 aircraft, and to obtain data on the composition (especially free-radical concentrations) and transport rates in the near-tropopause region of both the stratosphere and troposphere. Principal motivations were to help reduce uncertainties in the assessment of effects of stratospheric aviation on ozone and climate, and to understand long-term trends in ozone concentrations. The role of the Project Scientist is to plan the flights of the of the ER-2, attempting to match the science goals with the capabilities of the payload and aircraft, to provide liaison between the science team, aircraft operations, maintenance and engineering, and the Program Offices (Upper Atmospheric Research Program and High Speed Research Program), and to help the science team in collaborative efforts to analyze results.

Summary of Progress and Results

I have collaborated with co-project scientist Paul A. Newman. STRAT deployments were carried out in May and October 1995, February and July 1996, and are planned for September and December 1996, covering the Northern Hemisphere from the equator to 60°N. The observations build on the database from the Stratospheric Photochemistry, Aerosols and Dynamics Experiment (SPADE) and the Airborne Southern Hemisphere Ozone Experiment (ASHOE) to provide an unprecedented, comprehensive survey of tracer distributions, including the evolution over time scales from seasonal to approximately 5 years. The first comprehensive data on tracer distributions and atmospheric transport in the near-tropopause region, and extensive measurements of free radical concentrations in the upper troposphere, have been obtained.

The mission is in progress and new information is currently emerging.

Several results have been discussed in preliminary analyses:

- Data for CO_2 and SF_6 accurately define the mean age of stratospheric air, 5 to 6 years at middle altitudes. Mean age may be regarded as a pseudo-tracer in many respects analogous to exhaust from stratospheric aircraft, hence this measurement provides a critical new constraint for assessments of atmospheric impacts of stratospheric aviation.

- Tracer data show that the near-tropopause region at mid-latitudes (the so-called "middle world") receives inputs from the troposphere significantly different from the sources that supply the bulk of the stratosphere (e.g., higher water concentrations), confirming suggestions based on dynamical analysis by Holton and colleagues. The air in this region appears to be removed rapidly to the troposphere, since the anomalous tracer concentrations are never observed higher in the stratosphere. This result has important implications for exhaust from subsonic aviation, which enters the lowermost stratosphere during winter, but which will apparently not be transported into the bulk stratosphere.
- Concentrations of HO sub x and NO sub x radicals are significantly higher in the upper troposphere than predicted by current atmospheric models. This discrepancy is critical to assessments of aircraft impacts on the upper troposphere, and intensive study is underway to understand the contributing factors.

Publications

(The following are the publications in which I participated as an author, including those from my prior role as mission scientist for SPADE. Many dozens of other articles have been published from the SPADE and STRAT missions.)

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C. Global Chemical Modeling

Three-Dimensional Modeling of Chemical Constituents in the Global Troposphere

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Research Objectives

The goal of the project is to develop an off-line three-dimensional (3-D) chemical-transport model (CTM) capable of simulating the global distribution of chemical constituents in the global troposphere and lower stratosphere, coupled with a mechanistic model for surface emissions, taking into account biological processes on the continents and in the ocean, as well as anthropogenic effects.

Summary of Progress and Results

Development of the Model

We have developed a chemical-transport model called MOZART (Model of OZone And Related species in the Troposphere), by implementing a relatively detailed chemical code in a three-dimensional transport code driven by the NCAR Community Climate Model (CCM): we are now using the omega-version of the CCM, which will be the basis for its newest version under development, CCM3. The transport code, which has a resolution of 2.8 degrees in longitude and latitude, and 18 levels in the vertical includes advection, sub-grid diffusion and convection processes. The chemical code includes now approximately 40 species, involving more than 110 chemical and photochemical reactions. Photodissociation rates are calculated using look-up tables, which now takes into account the temperature dependence of the cross-sections, as well as the effect of cloudiness. A simple aqueous-phase chemical scheme has been developed in order to account for the solubility of certain chemical compounds and their reactions inside cloud droplets.

In the current version of the model, monthly mean distribution of surface emission and dry deposition distributions are represented according to the inventory of Muller [1992]. These distributions have been updated using, when available, fluxes from the GEIA inventory. We have also been working with Dr. Hao (U.S. Forest Service) to revise our estimates of the biomass burning emissions for several compounds. Emissions factors are now ecosystem dependent, and the seasonal variation is better represented.

One goal of the overall project is to couple the CTM with a relatively sophisticated emission model of biogenic gases driven by meteorological factors provided by the general circulation model. Using this

methodology, the release of biogenic gases should be consistent with the weather patterns in the atmospheric model. A model for isoprene and terpenes emission has been developed, using a methodology developed at NCAR. The net primary productivity is first derived for all months of the year. The seasonal variation of the phytomass is then calculated on the basis of global satellite observations, as well as on geographical distribution ecosystems. A canopy model is then used to calculate the emissions of isoprene and terpenes, as a function of temperature and the light inside the canopy, as well as measured emission factors and ecosystem type. The surface model has been coupled with an intermediate 3-D model of the troposphere and preliminary results have been obtained.

We have also been developing new graphic tools to visualize the output fields of the model. This code allows us to inspect easily and rapidly a large amount of data. It also provides an easy way to pint out problems with the model.

A first version of MOZART has been run over a period of two years, and the resulting chemical fields have been analyzed and compared against observations. Specifically, comparisons have been performed with observations made during the MLOPEX I and II campaigns, and a paper discussing the comparisons has appeared in the *Journal of Geophysical Research* special issue on MLOPEX. Data from several other field and aircraft campaigns have also been used to validate and verify the model. These comparisons have shown strengths and weaknesses of the first version of the model. Several improvements have been implemented, and a new two-year run of MOZART has just been completed. We are currently analyzing the results obtained from this new version of the model, and a detailed analysis of ozone and other trace gases budgets in the troposphere will be performed.

Scientific Studies

While MOZART is currently being developed, several scientific studies have been performed using, in most cases, an intermediate global transport-chemical model of the troposphere called IMAGES. We have studied the impact of biomass burning on the global distribution of carbon monoxide, methane, hydrocarbons and nitrogen oxides. An other study has assessed the causes for the observed reduction in the CO surface concentration during the 1990-1993 period. IMAGES has also been used to evaluate the potential impact of the current fleet of subsonic aircraft on tropospheric ozone.

Publications

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Budget of Nitrogen Compounds in the Global Atmosphere: Observations-Based Climatologies and Three-Dimensional Chemical-Transport Model Simulations

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Research Objectives

To investigate the global budget of nitrogen compounds in the atmosphere, using existing data in conjunction with three-dimensional (3-D) Chemical-Transport-Model (CTM) simulations. Climatologies of nitrogen compounds and related species (e.g., ozone) from airborne measurements and other field campaigns will be used and extended by more recent experiments which cover the upper troposphere and lower stratosphere.

The purpose of the project will be to identify and quantify the different contributions (sources, sinks, transport) to the NO_x budget. For this purpose, the observations-based climatologies will be used to evaluate the CTM. The model will be used to simulate the global distribution of nitrogen species and investigate the magnitude of the individual sources (including lightning, surface emissions and aircraft releases), transport processes and heterogeneous processes.

Summary of Progress and Results

The IMAGES (Intermediate Model of the Annual and Global Evolution of Species) model has provided the results that form a central component of Chapter 4 of the 1996 Interim Assessment for the SASS program. For that purpose, IMAGES has been used for comparison of the chemical mechanism with other chemical box models, for evaluation of the model transport performance by a Radon-222 study, comparison of the model results with O_3, CO, NO, HNO_3 and PAN measurements, and for sensitivity simulations of the nitrogen species and ozone distributions to lightning and aircraft emissions, convection, and non-methane hydrocarbons chemistry.

A global evaluation of a high resolution CTM called MOZART (Model of OZone And Related species in the Troposphere) has been initiated. As a first step, the model has been used to compare calculated abundances of chemical species and their seasonal evolution in the remote Pacific troposphere near Hawaii with values observed during the Mauna Loa Observatory Photochemistry Experiments (MLOPEX 1 and 2). Comparison of calculated HNO_3 and H_2O_2 seasonal variations and observations have been used to refine the washout and rainout parameterizations of soluble

species in the model. To complement the understanding of wet removal processes and the HO_x budget in larger scale models, we have begun an examination of available observations of formaldehyde, hydrogen peroxide and methyl peroxide in the remote atmosphere with a detailed box model.

Climatologies of tropospheric NO_x and NO_y have been compiled from data previously published. Emphasis has been on non-urban measurements and aircraft data. Model generated climatologies from six chemical transport models including MOZART have been compared to observations in the boundary layer and the middle troposphere for summer and winter. These comparisons test our understanding of the chemical and transport processes responsible for these species distributions. We have also contributed to the data analysis of *in situ* odd nitrogen measurements made on board the NASA DC-8 during the recent TOTE/VOTE projects. This data acquired over a broad geographic region in the upper troposphere and lower stratosphere, in combination with data from other projects, will provide valuable wintertime observations for comparison with the CTM.

The heterogeneous reduction of HNO_3 into NO on carbonaceous aerosols originally discussed by Lary *et al.* [*J. Geophys. Res.*, in press], has been introduced in a photochemical box-model on the basis of black carbon mass densities measured during MLOPEX 2. This recycling to NO_x decreases the HNO_3/NO_x ratio close to observed values and brings NO_x concentrations into better agreement with observations. Further laboratory and field measurements are required to confirm this process which might strongly impact the nitrogen and ozone budgets on a global scale.

Publications

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Transport and Chemical Characteristics of Tropospheric Trace Gas Cycles in East Asia

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Research Objectives

The transport and chemical characteristics of the regional trace gas cycles in East Asia with specific emphasis on ozone and mineral aerosols are investigated in this project. The project consists of three-dimensional regional-scale simulations of the transport and chemical processes affecting tropospheric chemistry in East Asia. Aerosols are an important feature of the troposphere over Asia and they play a significant, but yet unquantified, role in the trace-gas cycles in the region. Furthermore, dust, with a well characterized surface source, provides a valuable tracer which can be exploited to help quantify the tropospheric ozone budget in this region. A three-year project which continued the work on tropospheric ozone and also addresses the role of dust in the sulfate, nitrate and oxidant cycles in east Asia was initiated in the spring of 1994.

Summary of Progress and Results

The primary activities during this year of the project were two-fold: (1) the investigation of the relative role of transport vs. *in situ* tropospheric chemistry in determining the distribution of ozone in east Asia; and (2) evaluating the role of mineral aerosol in tropospheric chemistry. Activities related to these topics are discussed below.

We performed a series of 3-D model simulations focused on the roles of transport and chemistry in determining the distribution of ozone in east Asia. We chose the time period 1 through 13 May 1987 as our study period. Near-surface ozone observations in Japan showed that ozone levels went up significantly after the passage of the cold front with values reaching 100 ppbv. These high ozone levels were also accompanied by elevated mineral aerosol concentrations (as high as 100 mg/m^3). To investigate the roles of transport and chemistry in determining the distribution of ozone in east Asia we performed a series of model experiments.

The transport processes associated with the passage of the cold front were found to play a critical role in determining the spatial distribution of ozone. Strong downward fluxes of ozone from the upper troposphere towards the surface occurred behind the cold fronts and below the upper level low pressure troughs. High ozone levels were transported to 1 to 2 km above the surface by the high pressure systems which trail the cold fronts. These transport processes were able to account for many of the synoptic-scale features in the observed ozone filed at Happo, Japan. The photochemical production of ozone was found to be important in the regions over the precursor

source regions, and in the continental outflow zones. Calculated production efficiency for ozone, were found to be similar to those observed and calculated over North America. The regions of strong photochemistry were largely restricted to the lowest 2 km of the atmosphere. However in regions of convective activity the chemical production zones reach the mid troposphere. Ozone production on the regional-scale contributed up to 30% of the total ozone in the lowest 2.5 km of the study domain, and from 2 to 10% of the total ozone in the domain.

The second major activity of this past year was the investigation into the role of mineral aerosol in tropospheric chemistry. Our results illustrate that mineral aerosol can have a significant impact on the chemistry of the troposphere. In the case of sulfate, a significant fraction of sulfate is predicted to be associated with mineral aerosol. The regions where over 20% of the sulfate is associated with the mineral aerosol extends from east Asia to the central Pacific Ocean, and out into the Southern Hemisphere region of the Indian Ocean, spans from central Africa to the northeastern portions of South America, and covers vast regions of the western USA, southern South America, and Australia.

An even larger fraction of gas phase nitric acid may also be neutralized by mineral aerosol. The regions where at least 40% of the total nitrate is found on the mineral aerosol covers vast regions of the Northern and Southern Hemispheres. During the months of FMA the region covers almost all of Asia and extends throughout the central and northern regions of the Pacific Ocean basin, and the tropical and sub-tropical Atlantic and Indian Oceans. Only the regions of western and central Europe, the eastern parts of North and Central America, and the high latitude ($> 60^{\circ}$) zones are predicted to have relatively small portions of HNO_3 associated with the mineral aerosol.

Interactions of N_2O_5, O_3, and HO_2. radicals with dust were also found to affect the photochemical oxidant cycle, with ozone concentrations decreasing by up to 10% in and nearby the dust source areas. Comparison of these results with limited available measurements indicates that the proposed reactions can indeed take place, although the lack of measurements prevents a rigorous validation. The direct reaction of ozone on mineral aerosol warrants further study, and could be important at accommodation coefficients $> 5 \times 10^{-5}$. These effects can be intensified on regional-scales during high dust periods, where surface areas of the mineral aerosol can be an order of magnitude higher than the monthly averaged values calculated by the global model.

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Tropical Ozone Simulation

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Research Objectives

This research task has studied the maintenance of high concentrations of tropospheric ozone, a greenhouse gas, phytotoxin, and oxidant in regions seemingly remote from pollution. It was thought that the source of particularly striking accumulation of tropospheric ozone in the middle of the Equatorial Atlantic Ocean was due to biomass burning taking place in South America or Africa. However, the roles each played and the process for mid-oceanic, mid-tropospheric pollution were not clear. This project created a 3-D tropospheric chemistry model that assimilated the winds and weather which prevailed during NASA's airborne expedition, the Tropical Atmospheric Chemistry Experiment-Atlantic (TRACE-A). It also investigated chemical processes that could help explain continuing production of tropospheric ozone that are now widely recognized but are not represented in existing models.

Summary of Progress and Results

The maintenance of tropospheric ozone is a complex interplay of many chemical species and meteorological processes, and this project has made explicit several, while pointing out a remaining anomaly in our theory that is now widely recognized. The most visible concentration of tropospheric ozone in the mid-Atlantic appears to be due to the "Great African Plume," which extends up to about 6 km. This plume arises out of a convergence of polluted material in Equatorial and Southern Africa. Pollution is then lofted in the Inter-Oceanic Convergence of the region, by processes that involve intense boundary layer mixing and also convective clouds reaching to the upper troposphere. The lower tropospheric mixing process is the main source of slow, westward moving pollution episodes which produce maxima in tropospheric carbon monoxide and ozone just south of the Equator, and extend to the western tip of South America. Thunderstorm mixing of pollutants tends to lead to southeastward movement of these pollutants, and great pinwheeling plumes of carbon monoxide and ozone spin out from the central convective areas of Africa and especially South America, especially above 8 km.

Most ozone in our simulations seems to be made close to the source, over the continent, only a day or so downwind of the agricultural burning which is its source. Theory and models suggest that nitrogen oxides die out, and ozone production must then cease. Observation, however, has shown

the remainder of chemically significant concentrations of nitrogen oxides in the middle and troposphere. We have suggested that there is a "re-NO_x-fication" process which reproduces photochemically active nitrogen oxides, NO_x. Several pathways for this process are now being investigated in the laboratory.

Studies TRACE-A and accompanying intensive experiments pointed out that the source of the biomass-burning pollution was very poorly understood in detail. Our 3-D simulations showed that emissions near those which have been based on the Food and Agriculture Organization statistics, and other survey methods, are approximately correct, since they give appropriate airborne concentrations of carbon monoxide. However, our studies have provided a first very-large scale test of cumulonimbus venting parameterizations derived from meteorological models, also using CO concentrations as a tracers. Our parameterization, at least, appeared to be nearly 30% below the tracer evidence. We expect that all such parameterization used in climate and assessment models need more careful calibration.

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Chemistry-Transport Modeling of the Troposphere and Stratosphere and Interactions with Climate: Research Studies with and Continued Development of the LLNL Atmospheric Chemistry-Transport Models and the Coupling with a Climate Model

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Research Objectives

The objective of this project, over the three-year period, is to develop and apply a 3-D chemistry-transport model, built on the existing LLNL (Lawrence Livermore National Laboratory) IMPACT (Integrated Massively Parallel Atmospheric Chemistry and Transport, a 3-D advection/convection model based on a platform-independent message passing scheme for parallel computation) framework, with an initial emphasis on stratospheric processes. We will focus on NO_x chemistry in the lower stratosphere, its role in ozone change and in radical family behavior in this region, and its response to changes in aerosol loading. With the developed model, we will study ozone change as a climate forcing term, progressing toward interactive runs with climate models coupled through the framework, and increased capabilities in modeling tropospheric photochemistry and aerosols. We will also continue to support assessment activities for UNEP, IPCC, and NASA HSRP/AEAP, evaluating and implementing any additional required model capabilities in our 2-D model.

Summary of Progress and Results

We are currently early in the second year of funding on this project. We have accomplished our first full stratospheric diel photochemistry integration in three-dimensions, using NASA Goddard Space Flight Center Data Assimilation Office products for winds and convective mass flux. These test integrations have been performed on a single node of a vectorized supercomputer (Cray C90) and on multiple nodes of two different massively parallel platforms (Cray T3D and IBM SP2). Our approach is based on adapting a fast, accurate, variable time-step integrator (SMVGEAR 2, Sparse Matrix Vectorized Gear), developed by Mark Jacobson from the work of William Gear, to our model framework. Using this solution technique and taking advantage of parallel computing platforms, we can perform scientifically significant integrations without the need for family assumptions and their attendant uncertainties.

To support development of our intended technique, we recast our 2-D model to allow near plug-in module compatibility with the photochemical solution module of the 3-D model. With this model, we successfully demonstrated close agreement between our implementation and modifications of SMVGEAR 2 and our earlier, well-proven, GEAR-based non-operator-split solution technique.

The SMVGEAR 2 modifications were required to allow interaction with the three-dimensional domain decomposition scheme, with the order of operators in IMPACT, and with our chemist-user-interface photochemical mechanism preprocessor. This gives us the ability to investigate quickly new mechanisms while minimizing bookkeeping and typographical errors. We are currently using an on-line two-stream radiation package to calculate photolysis process frequencies, but are evaluating other techniques such as table look-up.

We have used early forms of IMPACT in conjunction with our 2-D model to investigate the effects of iodine-containing substituted methane compounds on the stratosphere and troposphere and to investigate partitioning of NO_x sources in the troposphere. Susan Solomon and coworkers have suggested that iodine may play a role in affecting lower stratospheric ozone trends. In advance of a full 3-D simulation, we have combined IMPACT and LOTUS to study the chemistry of CH_3I (a naturally emitted compound) and CF_3I (a proposed industrial compound). Because the species have short photochemical lifetimes of a few days, a 3-D transport model with convective mass flow is necessary to simulate the atmospheric distribution and particularly the abundance in air entering the stratosphere. IMPACT source distributions were calculated using zonal photolysis constants, then the distributions were zonally averaged and supplied to the 2-D photochemistry model. Convective delivery of iodine source gases to the tropopause region increases stratospheric iodine by more than an order of magnitude over predictions of the 2-D model with only advection and diffusion. Effects on ozone are in the range of earlier estimates, but probably substantially exceed their lower limits.

Using our 2-D model, we have also completed an extensive series of scenario calculations of the effects of High Speed Civil Transport and subsonic aircraft on ozone, including sensitivities to PSC-related processes, stratospheric chlorine burden, and newly identified reactions such as the heterogeneous hydrolysis of bromine nitrate on sulfuric acid aerosol surfaces. These results are reported in the *1995 Scientific Assessment of the Atmospheric Effects of Stratospheric Aircraft.* We are also collaborating with workers at SRI on kinetic uncertainty analysis using multivariate sensitivity analysis techniques.

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2-D Stratospheric Model - Radiation

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Research Objectives

We proposed to develop a hierarchy of accurate radiative transfer modeling methods for use in 2-D and 3-D chemical transport models. These methods are now being used by members of the Caltech and MIT stratospheric modeling groups.

Summary of Progress and Results

This task was dropped from the NASA Upper Atmosphere Research Program at the end of FY 1995, but we still had about 9 K (3 weeks) of carryover for FY 1996. This funding was used to finish a few ongoing tasks, and to provide salary support for reviews of papers and proposals. During FY 1996, I provided modeling support and performed validation experiments for the radiative transfer programs being used Janusz Eluszkiewicz, who is using these tools to analyze UARS MLS and CLAES data.

Publications

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3-D Chemistry and Transport Model

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Research Objectives

The goal of this project is to enhance our understanding of the chemistry and transport of the stratosphere. The strategy of the investigation is to construct models of the system guided by data analysis. Winds from the data assimilation are used to study chemistry and transport in the stratosphere and troposphere. This ensures that the transport is represented realistically, and permits clearer identification of chemical mechanisms which contribute to observed species behavior. A comparison of total ozone from a year long simulation with parameterized chemistry with TOMS observations attests to the credibility of the lower stratospheric transport. The simulation has been compared with UARS observations and also used to interpret balloon observations. The mid-latitude middle stratosphere ozone compares well with observations, and is shown to be influenced both by horizontal transport and photochemistry throughout the winter. Calculated tracer profiles at mid-latitudes compare poorly with observations, apparently showing problems with the vertical transport which will be considered further this year. Trajectory calculations are being used with model simulations and observations from satellite and aircraft to investigate the details of stratosphere/troposphere exchange in the CTM.

Winds from a mechanistic model are also used for transport; these have been used to examine the relative roles of transport and photochemistry in the behavior of odd nitrogen species following solar proton events, and interannual differences in chlorine effects on the ozone in the Northern Hemisphere polar lower stratosphere. These calculations are directed towards interpretation of SAGE NO_2 and TOMS total ozone data. Such calculations have also been used to explain wave driven changes in long lived constituents. These calculations have also motivated a higher upper boundary in the GEOS-1 model used in the data assimilation system.

Future plans include full chemistry integrations for several Northern Hemisphere winters to understand the photochemical and dynamical contributions to observed ozone variability. The full chemistry integration for November 1991 through May 1992 will be extended through September 1992 to examine the relevance of full 3-D transport and photochemistry to the upcoming POLARIS mission.

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Two-Dimensional Modeling Studies of the Middle Atmosphere

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Research Objectives

To study the processes that control photochemistry, radiative transfer, and transport in the middle atmosphere. Topics examined include the effect of planetary and gravity wave driving on the circulation of the middle atmosphere and the transport of minor species; the role of iodine compounds in ozone depletion; the effect on the middle atmosphere of CO_2 increases; and the effect of interannual variations in aerosol concentration (due to major volcanic eruptions) on the long-term trend of ozone depletion.

Summary of Progress and Results

- Work on the new Garcia-Solomon (GS) model, including new treatments of zonal mean and planetary wave dynamics, stratospheric and mesospheric photochemistry, and IR transfer was completed in 1994, and the results published in Garcia and Solomon [1994]. The model now uses an IR transfer code derived form the NCAR Community Climate Model below 70 km. Above 70 km, IR transfer can be parameterized as Newtonian cooling in order to expedite computations that do not require high accuracy in the mesosphere. Alternatively, a non-LTE band code has been developed and implemented within the GS model by R. Portmann (NOAA, Aeronomy Laboratory).
- The GS model has been used to study various aspects of the dynamics of the middle atmosphere. The planetary wave parameterization was validated by applying it to stratospheric circulation statistics [Randel and Garcia, 1994]. The effect of gravity waves on the temperature structure of the polar stratosphere was demonstrated to be important, especially in southern hemisphere winter [Garcia and Boville, 1994]; these results have important implications for the formulation of gravity wave drag in two- and three-dimensional models.
- The GS model was used to study the role of iodine in ozone depletion [Solomon *et al.*, 1994a] and the potential for ozone depletion and global warming of CF_3I [Solomon *et al.*, 1994b]
- The middle atmosphere impact of CO_2 increases was investigated by Portmann *et al.* [1995]. Interactions between IR cooling and gravity wave driving were shown to be important in determining the response of the mesosphere to changes in the CO_2 abundance.

- The most recent work has centered on the evaluation of the role of interannual aerosol variations on ozone trends. The importance of taking into account these ozone variations (associated, e.g., with large volcanic eruptions) has been demonstrated by Solomon *et al.* [1996] and Portmann *et al.* [1996].

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Use of Two-Dimensional Models for Understanding Atmospheric Processes

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Research Objectives

The objective of this research is to use two-dimensional (altitude and latitude) models of the atmosphere to investigate problems relating to the ozone depletion observed and the importance of the chlorine family in controlling ozone in the upper stratosphere, the effects of aircraft and space launch vehicles on the stratosphere, and the influence of the cycles in ultraviolet flux and energetic particles on the middle atmosphere.

Summary of Progress and Results

We have made improvements to our two-dimensional (2-D) model, have applied the model to several problems relevant to understanding ozone changes in the middle atmosphere, and have shared our model results with a group which has a balloon-borne instrument.

Polar stratospheric clouds are known to be very important in understanding polar processes. These are now included in our model in a parameterized way which uses climatological temperature variations.

Ozone depletion in the upper stratosphere has been well documented with satellite measurements. We have used our model to help understand the ozone decrease and have found that our model overpredicts the amount of chlorine-catalyzed loss of ozone in this region. We have found that inclusion of the $OH + ClO \rightarrow HCl + O_2$ reaction in our model calculations improves the agreement between our model results and measurements.

The influence of the 27-day solar rotation and the 11-year solar cycle ultraviolet flux variations on ozone have been assessed with our "fixed transport" model. Substantial changes in the ozone production by O_2 photolysis over the 27-day and 11-year periods drive the ozone changes in the upper stratosphere.

The influence of energetic particles on the middle atmosphere has been assessed with our model. We have predicted galactic cosmic ray and solar proton event caused odd nitrogen and ozone fluctuations over solar cycle timescales. We have also studied the shorter time scale effects of the massive solar proton events that occurred in October 1989. We have computed the effects on mesospheric OH and ozone during certain periods of precipitating relativistic electrons.

The impact on the stratosphere of a launch scenario of nine Space Shuttles and three Titan IVs has been assessed with our model. We predict that maximum chlorine enhancements will be 0.4%, maximum profile ozone decreases will be 0.14%, and maximum total ozone decreases will be 0.05%.

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3-D Models of Tropospheric Chemistry

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Research Objectives

The general goal of this project is to improve knowledge of the chemistry of the troposphere through the development and application of global 3-D models. We use 3-D models as a powerful tool for interpreting the distribution of species in the troposphere and for resolving the coupling between dynamical and chemical processes. The primary emphasis of our current work is to understand the impacts of human activity on tropospheric ozone and sulfate aerosols, and to assess the resulting implications for the oxidizing power of the atmosphere and for climate. Our strategy for the next few years includes: 1) incorporating tropospheric chemistry in a new-generation, high-resolution general circulation model (GCM) developed at the Goddard Institute of Space Studies (GISS), to investigate the coupling between chemistry and climate; and 2) using tropospheric chemistry simulations with assimilated meteorological data from the NASA Data Assimilation Office to interpret observations from field campaigns and test our understanding of atmospheric processes. A parallel component of our activity is to evaluate the representations of dynamical processes in global 3-D models using chemical tracers, with particular focus on convective mixing, interhemispheric exchange, and cross-tropopause transport.

Summary of Progress and Results

We have completed recently a global 3-D model study of tropospheric ozone and its precursors using the GISS GCM 2. The model includes comprehensive descriptions of emissions, chemistry, and deposition of trace gases. It captures well many features of the observed distributions of ozone, CO, NO_y species, and hydrocarbons. There are some regional discrepancies due in part to anomalies in the GISS GCM 2 meteorological fields; also, the ability of the model to describe the upper troposphere is hampered by coarse vertical resolution. We have tested in the model the need to include aqueous-phase cloud chemistry, prompted by previous model studies which suggested a large effect on ozone; we find in fact that the effect is negligible and argue that the past studies rested on inappropriate assumptions. In another model study under completion, we show that uncertainties in hydrocarbon chemistry have a significant impact on the global ozone simulation and attempt to place constraints on these uncertainties.

Despite its weaknesses, our current model offers a useful first-generation tool to study the factors controlling tropospheric ozone and the oxidizing power of the atmosphere. We find that tropospheric ozone is mainly produced within the troposphere (rather than transported from the stratosphere) and that production at all altitudes within the troposphere is important. We also find that the net effect of fossil fuel combustion and biomass burning is to increase global OH concentrations (i.e., increase the oxidizing power of the atmosphere), challenging the common view that combustion has decreased the oxidizing power of the atmosphere since pre-industrial times. The difference, we argue, reflects better accounting of combustion influences on ozone and NO_x in our model.

We have also completed a global 3-D model study of atmospheric sulfate and its precursors. We find that sulfate concentrations at northern mid-latitudes are highly sensitive to the supply of H_2O_2 as an in-cloud SO_2 oxidant, and that 30 to 50% of SO_2 emitted in the northern mid-latitudes continents affects sulfate on a global scale. The ocean source of dimethylsulfide (DMS) needed in the model to reproduce observed sulfate concentrations and deposition fluxes at remote marine sites yields DMS concentrations in the marine boundary layer that are too high by a factor of 2, suggesting the presence of a missing oxidant for DMS. Simulated sulfate concentrations in the free troposphere are lower than in previous global models and more consistent with the few observations available; in our model, transport of SO_2 and sulfate to high altitudes is restricted by scavenging in wet convective updrafts. Because DMS is not scavenged during convection, it provides in the model the principal source of sulfate in the upper troposphere (volcanoes are also significant at high northern latitudes). We are presently testing this model result by analysis of sulfate observations from the NASA SUCCESS aircraft campaign.

Our work with chemical tracers has included a collaboration with D. Koch (Yale) to use beryllium-7 and lead-210 as tracers of convective mixing in the GISS GCM 2. We found major discrepancies with observations in the tropics which we traced to the lack of entrainment in the GCM scheme for wet convection. More recent tests with the new-generation GISS GCM 2' (which accounts for entrainment) indicate considerable improvement. We have also led the analysis of results from an community intercomparison of twenty global models using radon-222 and other short-lived tracers. Results show that most established 3-D models simulate vertical mixing and synoptic motions in the troposphere to within the constraints afforded by observed seasonal statistics for radon. However, none of the models captures the observed variability of radon in the upper troposphere.

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Continued Development and Validation of the AER Two-Dimensional Interactive Model

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Research Objectives

The overall goal of the project is to improve and better quantify our understanding of the processes that control the distribution and abundance of stratospheric ozone and its sensitivity to either natural or anthropogenic influences. Results from 2-D chemistry-transport models (CTMs) have been used to provide information on the future behavior of ozone in the stratosphere. Since the transport circulation and temperature are fixed in these models, they cannot account for the effects of changes in these quantities, which could be modified because of ozone redistribution and/or other changes in the troposphere associated with climate changes. Interactive 2-D models, which calculate the transport circulation and temperature along with concentrations of the chemical species, could provide answers to complement the results from three-dimension model calculations. The research objectives are:

- To provide model results from the AER 2-D CTM for the WMO stratospheric ozone assessment report.
- To refine the treatment of physics for the troposphere in the AER 2-D interactive model both in the heating rates and wave-forcing from propagation of planetary waves, to better understand the chemistry-climate interaction, and to determine the effects on ozone from changes in these quantities under anticipated changes in the global environment.
- To perform diagnostic studies to assess the limitations of interactive 2-D models in providing assessment results. The studies will be based on a mechanistic model that simulate transport (in latitude and longitude) on isentropic surfaces which will be extended eventually to a 3-D mechanistic model.
- To study the role of ozone in climate-chemistry interaction by developing a 2-D coupled climate-chemistry model.

Summary of Progress and Results

Refinements of the 2-D Chemistry Transport Model: The vertical resolution has been increased by a factor of three, from 3.5 km to 1.2 km allowing us to better resolve the tropopause. The 2-D

chemistry-transport model can now employ two different types of atmospheric circulation. The "Global Diffuser" model represents the normal circulation of the AER model. The "Tropical Barrier" model has smaller horizontal diffusion in the equatorial lower stratosphere, creating a "barrier" to cross-tropical transport [Plumb, 1996: *J. Geophys. Res.*, in press] from the tropopause up to 34 km. Improvements to the photochemical package include adoption of the photolysis code of Professor Michael Prather (University of California, Irvine) and updating the reaction rate constants according to the JPL recommendation.

We have combined the AER chemical transport model for gas phase sulfur species with the aerosol microphysics code of Dr. Glenn Yue at NASA Langley to produce a 2-D model for stratospheric sulfate aerosol. The gas phase sulfur species are DMS, MSA, H_2S, CS_2, OCS, SO_2, SO_3, and H_2SO_4. Processes that convert gas phase H_2SO_4 to aerosol particles and modify the aerosol size distribution include homogeneous nucleation, heteromolecular condensation, and coagulation. Aerosols evaporate in the upper stratosphere, recycling H_2SO_4 gas that can photodissociate into SO_3 and eventually SO_2. Sedimentation rate, which is specified as function of aerosol size and air density, partially control the stratospheric residence time of aerosols.

Activities related to stratospheric ozone assessment: AER participated in the preparation of the UNEP report, *Scientific Assessment of Ozone Depletion:: 1994.* Malcolm Ko was the lead author for Chapter 6 "Model Simulations of Stratospheric Ozone." Debra Weisenstein contributed model results. Model-calculated total ozone for 1980, the calculated trend between 1980 and 1990 was compared with TOMS and SBUV observations. The effects of the Mt. Pinatubo volcanic eruption were simulated in model calculations by increasing aerosol surface area by a factor of 30 over background and then allowing it to decay with a time constant of one year.

The AER 3-Wave Interactive 2-D Model: The AER 3-wave model couples a semi-spectral dynamical model with a zonal mean chemistry transport model and a radiative transfer code. The model calculates the E-P flux divergence and the eddy diffusion coefficients for chemical tracers in terms of the amplitudes, their time dependence and phases of dynamical waves simulated in the model. The eddy diffusion coefficient for a chemical tracer contains a term related to the local chemical loss rate of the tracer. Compared with commonly used parameterized values, the model calculated eddy diffusion coefficients for chemical species are smaller, especially in subtropics. Therefore, some of the model results show the effects of the so called tropical barrier. In spite of the high truncation in the dynamical module (only three longest waves are resolved), the model has successfully simulated many observed characteristics of stratospheric dynamics and distributions of chemical species including ozone. The 3-wave model was used to investigate the feedback effects of the ozone change in response to a fleet of supersonic aircraft.

Three-Dimensional Tracer Transport Model: Vertical transport in isentropic coordinates is generated only by diabatic processes. Motions caused by adiabatic processes are absorbed into the motions of isentropic surfaces, which are the coordinate planes themselves. This provides much numerical simplification for both modeling and data analysis and is particularly useful in the stratosphere where the diabatic heating is relatively small and dominated by the radiative heating. We have developed a 3-D transport model in isentropic coordinates. The daily NMC temperature and geopotential data are used to define the location of isentropic surfaces and the Montgomery streamfunction. The horizontal velocities in the isentropic surface are calculated from the Montgomery streamfunction as the geostrophic winds or the "linear balance" winds. We are currently exploring different methods of calculating the diabatic motion off the isentropic surfaces.

The AER Interactive Climate Chemistry Model (ICCM): Changes in temperature structure resulting from increased anthropogenic emissions of greenhouse gases can significantly alter both dynamical transport and the oxidizing capacity of the atmosphere, and hence its final chemical composition. We have made substantial progress toward the development of such an interactive climate-chemistry (ICC) model. We finished the first step which is to couple the Ko *et al.* [*J. Geophys. Res.*, *98*, 20429, 1993] 2-D interactive chemistry-transport model to the AER 2-D climate model [MacKay *et al.*, 1996, submitted to *J. Clim.*] so that changes in climatic state variables (temperature, moisture, wind fields, and surface features and processes) are calculated interactively with calculations of atmospheric chemistry. Our next step is to obtain a better simulation of the coupling between tropospheric temperature and stratospheric dynamics by replacing the Ko *et al.* module with the AER 3-wave interactive model.

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Global Studies of the Sulfur Cycle Including Its Influence on Climate and Climate Change

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Research Objectives

Our research is aimed at quantifying the role of both natural and anthropogenic sources of sulfur on the forcing of climate, and on climate change. Our approach has been to use simplified descriptions of the sulfur cycle together with a simplified, but mechanistically-based treatment for the change in drop size associated with changes in aerosol concentrations within existing climate models. There are many uncertainties associated with the treatment of the sulfur cycle in present models, however, our aim is to build increasing more complete treatments so that estimates of forcing and climate change can be made more accurate. For example, most current climate models use simplified descriptions of the water cycle and a treatment of precipitation that requires a parameterization for the treatment of the aqueous conversion of SO_2 to sulfate aerosol. We are working towards treating these processes in a consistent manner with the climate model by converting our chemical transport model to run with a climate model that has prognostic water.

Summary of Progress and Results

We have developed a simple description of the sulfur cycle and compared the predictions of sulfate from that model to existing observations [Penner *et al.*, 1994]. This model used the anthropogenic sulfur inventories developed by Spiro *et al.* [1992] for SO_2 from industrial, fossil fuel, and biomass burning except over North America where the inventory developed by Benkowitz [1982] for fossil fuel and industrial SO_2 emissions was used. These inventories represent emissions for ~1980. The natural sulfur emission inventories from Spiro *et al.* [1992] were also used in our simulations except that the oceanic emissions of DMS were doubled to better reflect the mid-range of estimates [Penner, 1994]. This also provided a more reasonable simulation of observed sulfate concentrations in remote regions [Penner *et al.*, 1994].

The gas-phase reactions of DMS and SO_2 with OH assumed a background concentration of OH that was specified according to the latitudinally and seasonally varying calculated concentrations from the LLNL 2-D model [see Penner *et al.*, 1991]. (H_2S emissions are small relative to other

sources of sulfur and were assumed to undergo the same reactions as DMS with identical reaction rate coefficients.) The reaction rate coefficients were varied monthly according to the average temperature and pressure at each location in the model. Aqueous reaction of SO_2 to form $SO_{4=}$ in clouds was treated in a simplified manner. This process was assumed to have an average e-folding lifetime of 30 hours at 40°N at the surface in summer and was scaled, proportional to the square of the locally specified concentration of OH at other locations. This formulation is a simplified attempt to account for the observed seasonal variations in sulfate concentrations and wet deposition in North America, by assuming that the rate of formation of $SO_{4=}$ in clouds depends both on the frequency of interception of a cloud by an air parcel (average cloud-free periods vary from 10 to 80 hours and on the local concentration of H_2O_2 (which was assumed to be proportional to square of the specified concentration of OH). The formulation provides a reasonable account of the observed variations in both sulfate concentrations and deposition in precipitation in the Eastern U.S. [Penner *et al.*, 1994]. In Europe, observed seasonal wet deposition of sulfate shows less variation between summer and winter than the modeled deposition patterns, in part due to the increased winter emissions expected in that region which were not represented in the model.

The model has been used to develop an initial estimate of climate forcing by sulfate aerosols through both direct (i.e., scattering by aerosols) and indirect (i.e., change in droplet concentration and cloud optical properties by aerosols) forcing mechanisms [Chuang *et al.*, 1995]. In order to estimate this latter forcing mechanism, we developed a parameterization for use in the climate model which relies on the local updraft velocity, the chemical nature of the aerosol, and its size distribution [Chuang and Penner, 1994]. We have compared the predicted effective radius with satellite analysis of effective radius and shown that the parameterization of droplet size is in reasonable agreement with the data. However, we note that the predicted indirect forcing can strongly depend on the level of pre-existing aerosols represented in the model [Novakov *et al.*, 1996] and these are highly uncertain [Andrews *et al.*, 1995].

In a separate study, we also examined the climate response to forcing by anthropogenic sulfate aerosols [Taylor and Penner, 1994]. We performed three simulations to establish the pattern of climate response to (1) forcing by CO_2 only, (2) forcing by sulfate only, and (3) forcing by the combined CO_2 and sulfate fields. These were compared to a simulation with pre-industrial levels of CO_2 and sulfate. These simulation results have been used to examine whether there is an increasing similarity between the predicted pattern and the historical record of temperature change [Santer *et al.*, 1995, 1996]. We have also looked at whether a pattern correlation method can be used to better quantify the forcing [Penner *et al.*, 1996].

We are now in the process of improving our representation of the sulfur cycle by coupling the chemical transport model to the ECHAM climate model. This latter model includes a prognostic treatment of clouds and will allow us to examine whether model predictions are altered when a more realistic treatment for the aqueous transformation of SO_2 to sulfate is included in the model.

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Global Atmospheric Chemical Modeling

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Research Objectives

The primary objective of this research is to couple effectively the meteorology fields generated from either climate models or weather assimilation models with chemistry-transport models (CTMs). We need to diagnose and archive those atmospheric processes that transport and transform chemicals in the atmosphere.

A core effort involves work on the new GISS II-prime model, to build in an on-line CTM for long-term climate simulations (primarily GISS), to design the met-field archives and a user-friendly CTM (primarily UCI), and to apply this CTM to the simulation of tropospheric ozone (primarily Harvard). A secondary UCI connection is with the European Centre model through the University of Oslo; this model will use historical met-fields based on the EC analyses-forecasts. As part of CTM development, UCI is testing simple chemical models (e.g., linearizations) against observations and developing those that can be used within the GISS stratospheric model to follow the evolution of the 21st century climate and the possible changes in ozone and greenhouse gas lifetimes.

Summary of Progress and Results

The development and testing of the CTMs is documented in some regular journal papers acknowledging ACMAP. The Hall and Prather [1993; 1995] papers were the first modern evaluation of the propagation of the CO_2 into the stratosphere and the study of seasonal stratospheric tracer correlations in 3-D. The Jacob *et al.* [1996] paper documents the Second international WCRP intercomparison of CTMs.

The Price *et al.* [1996] papers develop a new inventory for lightning NO_x specifically for tropospheric CTMs.

Other work looked at photochemical processes or at new approaches for diagnosing the CTMs. The eigenvalue analysis (a.k.a. natural modes) [Prather, 1994; 1996] has been expanded and shown how to apply to 3-D models. The examination of measurements of O_3 and NO_y [Avallone and Prather, 1996] demonstrated that the calculated O_2 photolysis matches the production of ozone in the lower tropical stratosphere as expected. Danilin *et al.* [1996] examined the chemical feedbacks in Antarctic ozone loss, showing that removal of bromine enhances chlorine-catalyzed loss.

Occasionally one has the opportunity to reach out to the larger scientific community. In one case it was an invited review paper on atmospheric chemistry for the International Combustion Symposium that was reviewed and published. In other cases it was important to comment on the role of the Space Shuttle and use of ODPs, or on the "road not taken" if CFC use had been uninhibited. Both of the commentaries were a result of ACMAP support. ACMAP has also supported efforts in the assessment process, both ozone and climate. These massive, peer-reviewed reports are an important requirement of our community. For IPCC, I was lead author on two successive chapters, and for WMO/UNEP, I was a co-author on two separate chapters.

UCI has finished development of the new CTM II-prime and has given specifications and working copies back to GISS and Harvard for our collaborative work. Further, probably minor changes will be needed in the core CTM to allow it to implement the EC met-fields being produced by Oslo this coming year. Working closely with GISS we have implemented high-resolution, standardized (linear) chemistry within the GISS II-prime stratospheric GCM. This model now works with N_2O and CFC-11 and will soon be tested with ozone so that chemical-dynamical coupling can be included in long-term climate simulations.

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Interpretation of Trace Gas Data Using Inverse Methods and Global Chemical Transport Models

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Research Objectives

This is a theoretical research project aimed at:

- Development, testing, and refining of inverse methods for determining regional and global transient source and sink strengths for long lived gases important in ozone depletion and climate forcing.
- Utilization of inverse methods to determine these source/sink strengths which use the NCAR/Boulder CCM2-T42 3-D model and a global 3-D Model for Atmospheric Transport and Chemistry (MATCH) which is based on analyzed observed wind fields (developed in collaboration by MIT and NCAR/Boulder).
- Determination of global (and perhaps regional) average hydroxyl radical concentrations using inverse methods with multiple titrating gases; and,
- Computation of the lifetimes and spatially resolved destruction rates of trace gases using 3-D models.

Important goals include determination of regional source strengths of methane, nitrous oxide, and other climatically and chemically important biogenic trace gases and also of halocarbons restricted by the Montreal Protocol and its follow-on agreements and hydrohalocarbons used as alternatives to the restricted halocarbons.

Summary of Progress and Results

We have pursued development and testing of two types of global 3-D chemical transport models. One type is based on the NCAR CCM2 climate model whose transport we have tested by simulating CCl_3F and comparing the results with ALE/GAGE observations [Hartley *et al.*, 1994]. The CCM2 does simulate some key features such as the structure (but not timing) of pollution events but there are shortcomings in other areas (e.g., cross-equatorial flow, storm track positions). The CCM2-based model has also been used to test the sensitivity of trace gas simulations to regional emission patterns [Hartley *et al.*, 1996]. The other type is based on using analyzed observed winds in the MATCH model developed in collaboration with NCAR. As a precursor to the latter development we tested several moist convection and boundary layer schemes using simulations and observations of chemical tracers [Mahowald *et al.*, 1995]. Initial

development of the MATCH model using selected schemes from the latter study has been completed and MATCH has been tested using both short-lived (^{222}Rn) and long-lived tracers [Mahowald, Ph.D. thesis, 1996].

We have continued our studies of the usefulness of inverse methods in 3-D models to deduce amplitudes of chemical sources and/or sinks [Prinn and Hartley, 1995; Mahowald Ph.D. thesis, 1996]. A comprehensive global process-oriented model for predicting emissions of nitrous oxide and methane has been developed, incorporated into a coupled chemistry-climate model, tested using atmospheric trace gas observations, and applied to ice-age and doubled-CO_2 climates [Liu, Ph.D. thesis, 1996]. Finally, we have recently completed development of a 3-D mesoscale model for chemistry and aerosols based on the UKMO mesoscale model and applied to a study of the role of aerosols in radiative forcing and identification of key uncertainties regarding aerosols [Pan, Ph.D. thesis, 1996].

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Systematic Assessment and Analysis of Two-Dimensional Stratospheric Ozone Models

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Research Objectives

This research addresses the quality of stratospheric ozone model predictions by merging the NASA Goddard Space Flight Center 2-D Stratospheric Photochemistry Model with a family of sensitivity analysis techniques and associated guided statistical methods. These tools provide a systematic and quantitative assessment of the model components controlling predicted ozone profiles.

Special attention is being given to the role of homogeneous chemistry, heterogeneous chemistry, and transport processes. The analysis methodology allows for: 1) quantitative assessment of the uncertainty in model predictions of ozone distributions; 2) identification of key species, chemical pathways, and kinetic rate parameters controlling ozone; 3) evaluation of cooperative effects among the various important species; 4) evaluation of the sensitivity of critical features in the ozone distribution to model parameters, reactions, and transport characteristics; 5) identification of potentially important missing model components; 6) prioritization of laboratory and field studies according to which would be most likely to result in a significant model improvement; and 7) construction of a reduced complexity, but accurate, chemical package suitable for inclusion in a global 3-D stratospheric model.

Summary of Progress and Results

A detailed chemical kinetic analysis of stratospheric models has been achieved through the development of new model analysis tools and their application to both 0-D and 2-D atmospheric chemistry models. In addition, the transport factors controlling atmospheric dynamics has been examined in a 2-D model. Aspects of this work has been carried out in collaboration with Drs. J. Shorter, C. Jackman and D. Considine. A summary of the research is given below.

- *Determination of key kinetic parameters:* A sensitivity analysis on stratospheric chemistry models determined which reactions strongly influenced ozone. This information, coupled with the suggested reaction rate uncertainties, identified the reactions that most significantly contribute to the total model uncertainty as: (1) $HO_2 + O_3 \rightarrow OH + O_2 + O_2$; (2) $N_2O + O(^1D) \rightarrow NO + NO$; (3) $OH + HO_2 \rightarrow H_2O + O_2$; (4) $O(^1D) + M \rightarrow O + M$; and (5) $H_2O + O(^1D) \rightarrow OH + OH$.

- *Model Ozone Uncertainty:* The uncertainty in chemical rate constants or the presence of a range of operating scenarios (e.g., aircraft number, emissions rates, etc.) lead to a distribution of ozone predictions. A new Guided Monte Carlo (GMC) technique has been developed for this purpose. The GMC technique provides a physically and mathematically based algorithm for reducing the expense of probabilistic analyses. We have calculated 0-D total model output uncertainty based on the uncertainties of both photolytic and chemical reaction rates and 2-D model output uncertainty based on the uncertainties of chemical reaction rates. For example, at 45°N latitude for 0-D, the total ozone model output uncertainties at 20, 30, and 40 km are 35%, 24%, and 24%. The 2-D model uncertainties varied between 5 and 20% in the main ozone region. The difference in the 0-D and 2-D results is attributed to photochemistry and transport.
- *Encapsulation of a 2-D model:* An approach has been developed to encapsulate the complex input-output response behavior of a model into a Fully Equivalent Operational Model, FEOM. The FEOM can rapidly learn the input-output behavior and then directly replace the original model. Using this approach, we developed a FEOM for the NASA 2-D atmospheric chemistry model which predicted ozone values for 250 Monte Carlo sampled input parameter sets to 90% accuracy compared to the full 2-D model calculated results, in the main ozone region. The FEOM requires a negligible amount of computer time for essentially the same result. The key to the FEOM is the decomposition of the model's response surface into a rapidly convergent series of low dimensional correlated functions.
- *Factors controlling atmospheric dynamics:* A functional sensitivity analysis has been performed on a 2-D Carbon-12 atmospheric tracer model. Sensitivity studies were pursued with respect to the advection field, diffusion coefficients, initial conditions, and boundary conditions. All of these sensitivities were related to the atmospheric dynamics Green's function. Distinct sensitivity behavior was found in the northern and southern latitudes.

Publications

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Global Modeling of Tropospheric Trace Gases

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Research Objectives

This work has three main goals: optimizing the GISS GCM for modeling of tropospheric trace gases; providing the necessary fluxes/parameters to Harvard and UCI for CTM studies; and investigating budgets of tropospheric species. Passive tracers are being used in the course of model development to determine transport properties of concern for tropospheric chemistry, including interhemispheric transport, vertical mixing within the troposphere, and tropospheric-stratospheric exchange. With a new version of the model, three hourly values of some 20 parameters, including winds, convective fluxes, temperatures, clouds, and rainfall were saved from a one-year simulation and provided to Daniel Jacob (Harvard) and Michael Prather (UCI) for their global chemical modeling tasks. Tropospheric budgets which are being investigated include NO_y, CO_2, and cosmogenic and radon-product isotopes for which rainout and scavenging parameterizations have been developed.

Summary of Progress and Results

During the past three years, we have implemented a procedure to test the transport processes of the GISS GCM as each major change is implemented into the model. The rationale is to ensure that new versions of the model are suitable for tropospheric chemistry purposes and to help in model development. This has involved adding on-line tracer capability, so that tracers are moved each time-step by the model dynamics, and sources/sinks incorporated each physics time step. The on-line tracers routinely used have included CFC-11, ^{85}Kr, ^{222}Rn, and ^{14}C. The first two tracers test interhemispheric transport, the third tests vertical mixing within the troposphere, and the fourth, stratospheric-tropospheric exchange.

Tests were performed as each of the following processes were improved in the GCM: boundary layer parameterization; convection; land surface; large-scale clouds; heat and moisture advection - the quadratic upstream scheme; and momentum advection (now using a fourth-order scheme). The results showed that the improved parameterizations for the boundary layer and convection reduce the model's interhemispheric exchange time to values close to observations (it was previously a factor of two too large). The improved numerical schemes provide for somewhat greater intra-hemispheric transport, as extratropical cyclones move more rapidly (and accurately). The new convection scheme also reduces the vertical mixing within the troposphere in the tropics, to values

more consistent with CTM (chemical tracer model) results from other models. Results of this work are described in Rind and Lerner [1996].

With a new version of the model incorporating these various changes, some 20 parameters, including winds, convective fluxes, temperatures, clouds, and rainfall were saved on an hourly basis for the two solstice months to investigate the desired temporal resolution for CTMs. It was concluded that for most parameters a three-hour averaging was sufficient, and a one-year simulation of these values was provided to Daniel Jacob (Harvard) and Michael Prather (UCI) for the next version of the GISS/Harvard and GISS/UCI CTMs. One hour values were provided for some parameters (e.g., boundary layer height) for special studies.

The tropospheric budgets of different species are being investigated. As part of the SASS exercise, NO_y distributions associated with lightning, stratospheric chemistry, surface sources, and aircraft were simulated on-line with the new version of the model and compared with results from CTMs. The lightning parameterization was developed in a series of studies with C. Price. The main differences arose from differing vertical resolution among the models, which affected the altitude of source location. These results will be included in the SASS 1996 interim assessment report. Vertical resolution also affected the distributions of ^{222}Rn and ^{14}C resolution in model tests; the optimal resolution is being explored with additional tracers, as described below.

Cosmogenic radionuclides (e.g., ^{7}Be, half-life 53 d) and radon-products (e.g., ^{210}Pb, half-life 23y) were used to investigate stratospheric-tropospheric exchange and atmospheric scavenging (in-cloud and rainout). In simulations with an off-line version of the old GISS model, ^{7}Be surface air concentrations in the tropics were considerably higher than observed. The discrepancy is most likely due to excessive convective vertical mass fluxes, lack of cloud entrainment, or lack of cloud anvils. A description of this work is currently in-press [Koch *et al.*, 1996].

The new version of the model includes these processes, and additional tests have been made of ^{7}Be and ^{210}Pb. Alterations were made in the parameterizations for: large-scale cloud scavenging rainout; evaporation of tracer as large-scale rain evaporates in layers below; the tracer mass in a convective plume reduced by in-cloud scavenging; evaporation below moist convective rain; convective up-draft mass-flux; convective down-draft mass flux; and up-draft entrainment. The experiments were able to improve the statistics for one or another of the tracers; this procedure will therefore allow the model's scavenging to be calibrated, which will be of use for future on-line aerosol experiments. A paper describing this work is being prepared for publication. Since the cosmogenic radionuclides have stratospheric sources, the results are also highly sensitive to model vertical resolution (and potentially model top location); simulations making use of several cosmogenic radionuclides of varying half-lives (^{7}Be; ^{32}P: $t_{1/2}$ = 14 d; ^{22}Na: $t_{1/2}$ = 22 y; ^{10}Be: $t_{1/2}$ = 10^6 y) will be explored in up-coming sensitivity studies.

In an attempt to investigate both the model's transport characteristics and the "Missing Sink" of atmospheric CO_2, carbon budget studies have been performed with proposed anthropogenic, biospheric and oceanic sources/sinks. The model's pole-to-pole gradient is twice as large as observed, a common model problem which has led to the proposition that there is an unknown Northern Hemisphere carbon sink (from the CFC-11 and ^{85}Kr studies we know that the model's interhemispheric transport is approximately correct). Additional sensitivity experiments and comparisons with other models are currently being performed.

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Stratospheric General Circulation Climate Models

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Research Objectives

This work has two main goals: to utilize the GISS Global Climate Middle Atmosphere Model (GCMAM) for studies of stratospheric climate change; and to develop the next version of the GCMAM with on-line photochemistry for coupled climate/chemistry simulations. During the past three years, the GCMAM has been used for published stratospheric climate studies involving changes in stratospheric ozone, stratospheric water vapor, aircraft releases of upper tropospheric water vapor, the quasi-biennial oscillation, and solar ultraviolet radiation. Work is in progress investigating the climatic impact of the ozone hole and the coupled CO_2-ozone climate change, and the effect of hemispheric asymmetries in stratospheric aerosols. Results of the climate change experiments are compared to natural variability with the use of an off-line microwave processor and satellite observations. Development has continued on the next version of the GCMAM which is nearing completion; it has 31 levels, 4° x 5° resolution, altered numerical schemes for heat, moisture and momentum advection, new parameterizations for the boundary layer, convection, clouds and the land surface, and a new gravity wave drag parameterization. On-line tracers have been added to the model, and preliminary studies are underway utilizing N_2O and CFC-11 to test transport within the stratosphere; CO_2 and SF_6 to test tropospheric-stratospheric exchange; and ^{14}C, and ^{7}Be to test stratospheric-tropospheric exchange. Fluxes and other parameters from the new model will be provided to Michael Prather at UCI for the next version of the GISS/UCI stratospheric CTM.

Summary of Progress and Results

The GISS GCMAM has been used for a variety of stratospheric climate change studies. The results from alterations in atmospheric carbon dioxide and volcanic aerosols, as well as the radiative forcing of various stratospheric constituents were published prior to this three-year period. The focus of recent work has been on stratospheric climate changes associated with ozone and water vapor perturbations. Ozone reduction experiments included removing ozone from the lower stratosphere entirely, and modifying ozone based on assessments of supersonic aircraft impacts. The results showed that stratospheric ozone changes are less effective in influencing climate than would be suggested by its radiative forcing at the tropopause, since alterations in the temperature lapse rate and cloud cover limit the surface feedbacks associated with high altitude forcing. Stratospheric water vapor experiments included doubling the stratospheric water vapor

content, and increasing it by 7% (consistent with estimates of the effect of supersonic aircraft); in addition the GCMAM was used to simulate the effect of subsonic aircraft water vapor release in the upper troposphere. All experiments showed that the stratosphere-climate connection consisted of the following pathways: the radiative forcing of the troposphere by the change in stratospheric constituents; the resulting change in tropospheric dynamics; the effect of the altered tropospheric dynamics on the stratosphere (a secondary stratospheric response); and the resulting tropospheric/climatic impact of the secondary stratospheric response. With the forcings used, the secondary response was often of the same magnitude as the primary radiative effect. This work was partially funded by AEAP/HSRP.

The complex stratospheric-tropospheric climate interactions were also apparent in experiments performed with a QBO and altered UV radiation. The model produced a realistic response to an input QBO forcing. When the QBO was combined with a 5% change in insolation at wavelengths less than 0.3 microns (a radiative forcing which itself produced only a small direct impact on the stratosphere), the resulting secondary stratospheric and tropospheric responses were surprisingly similar to published assessments of QBO/solar cycle effects in both the stratosphere and troposphere. This work was partially funded by the National Science Foundation.

A further effect of ozone changes is being considered in two experiments currently in progress. In the first experiment, a 1-D photochemical model for the Southern Hemisphere polar stratosphere is used to calculate ozone depletion at each grid box. This is input to the GCMAM, which responds by altering its temperature (and winds). The results are then assessed by the 1-D model which further alters ozone, which is again fed-back to the GCMAM, etc. The coupled time-stepping procedure shows the effects the ozone hole has on model temperatures/dynamics, and the 1-D model assesses how the changes in temperature affect the ozone hole. Relatively realistic results have been generated for ozone-temperature feedbacks as well as the progression of effects with time, latitude and altitude due to alterations in model dynamics.

In a second set of experiments, stratospheric ozone responses to changes in temperature and radiation were generated based on the 1-D photochemical model applied at various latitudes. Atmospheric CO_2 was doubled for both the troposphere and stratosphere (and sea surface temperatures allowed to adjust), and the experiment run twice: once with and once without the temperature-ozone response. Doubled CO_2 causes substantial cooling in the upper stratosphere, which has the effect of increasing ozone concentrations, and mitigating the cooling somewhat; there is also substantial warming in the upper troposphere/lower stratosphere, which has the effect of reducing ozone concentrations there. The net effect on the troposphere with the ozone adjustments is minimal. The results of these experiments will be presented at the SPARC meeting later this year.

For all of these experiments the question of when a climate change signal would become visible has been assessed by utilizing an off-line microwave processor to compare GCM results with natural variability as observed by the Microwave Limb Sounder (MSU). A new version of the GCMAM is nearing completion. It is being tested with on-line tracers to investigate stratospheric transport, and stratospheric-tropospheric exchange. Photochemical loss tables for CFC-11 and N_2O were generated by Michael Prather. The tracers utilized include those which will be part of the up-coming Models and Measurements 2 exercise. Winds, convective fluxes and other parameters from this model will be delivered to UCI for the next version of the stratospheric CTM this fall.

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Two-Dimensional Model Studies of Ozone Response to Global Changes

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Research Objectives

The overall goals of the project were: a) to continue refinement and testing of the AER two-dimensional model and its components through comparison to appropriate atmospheric measurements, and b) to utilize this model in studies of the impact of anthropogenic activities on the stratospheric ozone layer, particularly the hydrochloro/fluorocarbons introduced as substitutes for the CFCs. Specific areas of research included: a) quantify the effect of polar processes on the mid-latitude stratosphere; b) refine our understanding of heterogeneous processes occurring on the global sulfate layer; c) to assess impact of changes in tropospheric composition on ozone assessment predictions, as well as potential impact of substitutes on the tropospheric environment; d) to validate model results utilizing available satellite, aircraft, and ground-based measurements; and e) to participate in assessment efforts and reports as required by NASA.

Summary of Progress and Results

Stratospheric Ozone Assessment: AER participated in the preparation of the 1994 UNEP report, *Scientific Assessment of Ozone Depletion*:. Malcolm Ko was the lead author for Chapter 6 "Model Simulations of Stratospheric Ozone." Debra Weisenstein contributed model results. Model-calculated total ozone for 1980, the calculated trend between 1980 and 1990 was compared with TOMS and SBUV observations. The effects of the Mt. Pinatubo volcanic eruption were simulated in model calculations by increasing aerosol surface area by a factor of 30 over background and then allowing it to decay with a time constant of one year.

Evaluation of Heterogeneous Chemistry after the Pinatubo Eruption: We incorporated aerosol surface areas derived from SAGE-II observations to calculate the chemical perturbations induced by enhanced heterogeneous conversion after the eruption of Mt. Pinatubo. Our calculations yielded maximum ozone reductions during the 1992-1993 Northern Hemisphere winter. The delay response was due to a combination of the non-linear nature behavior of the heterogeneous reaction as a function of surface area, and the long time constants of ozone in the lower stratosphere. Results were published in Rodriguez *et al.*, 1994. We also compared our calculated column densities of NO_2 and HNO_3 to measurements at Lauder, New Zealand prior to and after the arrival of the Mt. Pinatubo cloud. Although there was qualitative agreement between the calculated and

observed temporal evolution of these column densities, the observed reduction in NO_2 and increase in HNO_3 was larger than calculated. Results were reported in Koike *et al.*, 1994.

Model simulations showed higher concentration of HNO_3 and smaller N_2O_5/HNO_3 ratios between 25 km to 30 km in 1992 than in 1985 because of the enhanced aerosol surface area due to Pinatubo eruption. The results are consistent with the measured profiles of HNO_3 and N_2O_5 from the ATMOS instruments taken in 1985 and 1992. Measured values of $ClONO_2$ from the ATMOS instrument are smaller than model calculated values both in 1985 and in 1992. This issue is unresolved at this point. Comparisons are reported in Rinsland *et al.*, [1994a, b].

Evaluation of Chemical Processes in the Polar Regions: We evaluated the coupling between bromine and chlorine compounds during the Antarctic ozone hole period inside the polar vortex. Due to the low levels of NO_x, the abundance of bromine compounds impacts the conversion of active chlorine to HCl in early spring. As bromine levels decrease, the magnitude of the chlorine-catalyzed ozone loss increases to take up the slack. The local relative efficiency of ozone destruction per bromine atom relative to that per chlorine atom (alpha-factor) ranges from 33 to 55 if total bromine decreases from 25 to 5 pptv. Results were reported by Danilin *et al.* [1996].

Modeling of the Behavior and Distribution of Source Gases: Model results were compared with the measured values of COF_2, HF and HCl from the ATMOS instrument in 1985 and 1992; and with the ground-based measured trend of HCFC-22. The results are consistent with the total chlorine and fluorine budget calculated using the emission data in the last several decades [Zander *et al.*, 1994].

Observations showed that the mixing ratio of SO_2 increases with altitude above 35 km. Our model simulations showed that this is consistent with the assumption that photolysis of gas-phase H_2SO_4 yields SO_2 as a product [Rinsland *et al.*, 1995].

Three-Dimensional Evaluation of the Concentration of Trifluoroacetic Acid (TFA) in Rainwater: Trifluoroacetic acid, a byproduct in the tropospheric degradation of the CFC-substitutes HFC-134a, HCFC123, and HCFC124, is not easily degradable in aquatic environments, and increasing concentrations could be deleterious to some plant life. We utilized the 8x10 version of the three-dimensional model CTM provided by M. J. Prather (UC Irvine) with simplified chemistry to calculate three-dimensional concentrations of TFA in rainwater. Our results show that concentrations close to 1 microgram/liter could be possible in certain dry regions, leading to potential accumulation in isolated aquatic environments. Results of these simulations will be submitted to Journal of Geophysical Research [Kotamarthi *et al.*, 1996].

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Air Quality Models for Atmospheric Chemistry

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Research Objectives

The overall objective of this project has been to develop and apply a state-of-the-science global tropospheric chemistry model. A major feature of the project has been to utilize experience and technologies developed in the use of comprehensive regional-scale atmospheric chemistry models in the development of the global chemistry model.

Summary of Progress and Results

Global Chemical/Aerosol Modeling: In a project funded partially by this grant, a 3-D tropospheric chemistry/aerosol model was developed and coupled with the global general circulation model CCM2 in order to estimate the direct and indirect radiative impact of anthropogenic aerosols on our planet's radiative balance. The major portion of the work funded by this grant consisted in tasks associated with the chemistry model. Two chemistry versions have been developed for this project: (1) a simplified chemistry version with prescribed concentrations of several major species (ozone, nitrogen oxides, and methane); and (2) a comprehensive chemistry version including full simulation of all important species. Under this grant, the simple chemistry version of the model was modified to include sulfur chemistry important for the simulation of atmospheric aerosols. Additionally, for the comprehensive chemistry version, an investigation of ordinary differential equation numerical solvers was carried out to select an appropriate numerical method for the integration of the chemical rate equations in the model. Development and application of the coupled chemistry-aerosol-climate model currently continues under separate grants. An additional task that was partially funded from this grant was the participation of one of the co-investigators (RDS) in a review of the current state-of-science and future direction of 3-D tropospheric chemistry models.

Carbon Monoxide Modeling: A 3-D tropospheric chemistry model was developed and used to model the global distribution of carbon monoxide (CO) during NASA's Measurement of Air Pollution by Satellites (MAPS) experiment which took place 5-13 October 1984. The MAPS experiment consisted of a gas-filter radiometer, tuned to measure CO in the mid-troposphere, which was placed on board the U.S. Space Shuttle. In a nadir-viewing mode, the radiometer measured upwelling radiance from the earth's surface, from which the column-weighted average

CO mixing ratio was inferred through a data reduction procedure. The MAPS measurements represent one of the first datasets gathered by satellite for a tropospheric trace species with such widespread global coverage over a relatively short time period. In a project partially funded by this grant, we have simulated the global tropospheric distribution of CO during this MAPS measurement period. Meteorological data for September through October 1984, were obtained from the European Centre for Medium-Range Weather Forecasting and used to drive the transport model. A simplified chemical transformation scheme was developed and an effective CO emissions inventory was created. Simulations for this time period indicate that biomass burning CO emissions from Africa and South America exert a large influence on CO levels in the Southern Hemisphere, and that convective cloud transport is a major process controlling the distribution of CO in the mid- and upper-troposphere. Comparisons of model results with MAPS satellite data as well as with *in situ* measurements indicate that our initial biomass burning CO emissions estimates for central and southern Africa may be substantially underpredicted; simulation results where CO emissions from these regions were doubled agree better with available measurements than do our base-case simulations. These results point out the difficulty and uncertainty in estimating the magnitude of emissions from biomass burning sources, although the impact of trace-gas emissions from these sources may be significant in the Southern Hemisphere.

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Zonally Averaged Model of the Chemistry, Radiation and Dynamics of the Atmosphere

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Research Objectives

Through theoretical and modeling studies, we aim to understand the processes that determine the present-day distribution of atmospheric ozone and other trace species and to assess potential perturbations. We have constructed a 2-D model in isentropic coordinates with comprehensive radiative transfer, fairly complete O_x, NO_x, Cl_y, HO_x chemistry and coupled self-consistent dynamical transports. Further development and calibration of the model are proposed for the purpose of assessing changes in stratospheric ozone, both for the recent past and for future scenarios.

Summary of Progress and Results

In prior years of this research project, we demonstrated our model's ability to simulate the latitudinal-height distribution of many long-lived chemical species in the atmosphere. During the last year of the project, our emphasis was on the year-to-year variation of ozone. In particular we were interested in assessing how much of the year-to-year changes in column ozone over the globe can be attributed to the extratropical QBO phenomenon. We have found that, when the linear trend and solar cycle variations are removed, a surprisingly large fraction of the variability in the extratropics can be attributed to the phenomenon of extratropical QBO, which we have established observationally to be real (statistically significant).

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Assessing the Role of Coupling between Chemistry and Climate

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Research Objectives

The primary objective is to better understand the coupling between global atmospheric chemistry and climate, and the impact of this coupling on concerns about global changes to ozone and climate. Studies are aimed at improving our understanding of the effects of human-induced emissions on tropospheric and stratospheric chemistry while at the same time addressing how interactions with climate processes and changes occurring to climate could affect the chemistry being evaluated. We are continuing development and updating of the 2-D model, generally in context of supporting our new 3-D model, but also for specific application studies to better understand atmospheric processes. The 3-D chemical-transport model development is a particular focus with emphasis on the treatment of chemistry in this model and in studies to validate the model.

Summary of Progress and Results

National and international assessments on ozone and climate have provided a special focus for our analyses of the interactions between atmospheric chemistry and climate. We were lead authors on the 1994 international ozone assessment [Solomon *et al.* in WMO, 1994], the Intergovernmental Panel on Climate Change assessments in 1994 and 1995 [IPCC, 1995, 1996], the NASA assessments on effects of global aircraft emissions [Friedl *et al.*, 1996; Stolarski *et al.*, 1995], and the current special assessment on climate and the human dimension [Wuebbles and Rosenberg, 1996]. We provided modeling results for these studies, plus evaluations of indices for ozone (Ozone Depletion Potentials) and climate (Global Warming Potentials) that involve analyses of the chemistry and climate responses [see also Wuebbles, 1995a, b]. Calculations from our chemistry-transport model and the NASA GISS GCM are being used in joint studies to examine the effects on climate resulting from aircraft emissions; at this point, these studies suggest that changes in tropospheric ozone and soot concentrations from current aircraft have little direct effect on climate.

Our zonally-averaged chemical-transport model continues to be used in studies of atmospheric processes, particularly relating to the stratosphere. It has been used to explain effects on ozone expected from the Pinatubo volcanic eruption [Kinnison *et al.*, 1994b], to examine possible effects of excited oxygen chemistry on stratospheric ozone (a new study is underway, but the prior Patten

et al., 1994, study did not find much effect), effects from aircraft emissions [e.g., Wuebbles and Kinnison, 1996] and to examine the relationship of important stratospheric species in comparison with measurements from the Upper Atmosphere Research Satellite (UARS) [Roche *et al.*, 1994]. We continue to push the capabilities of such models to better represent understanding of atmospheric processes [see Li *et al.*, 1995; Choi *et al.*, 1995; Kinnison *et al.*, 1994a; Considine *et al.*, 1996]. The model is also part of the ongoing analyses of trends in ozone and temperature in cooperative studies [e.g., Miller *et al.*, 1995a, b, c]. Analyses of satellite datasets in examining the relationship between volcanic eruptions, resulting stratospheric aerosols and upper tropospheric clouds are ongoing [see Song *et al.*, 1996].

Development of the new 3-D chemical-transport model of the troposphere and stratosphere is continuing. The NASA Goddard DAO dataset for the meteorology is working well in the model and tracer analyses are ongoing. We are coordinating with LLNL in incorporating the chemistry into the model with current focus on stratospheric processes and calculation of the 1990s atmosphere. First publications with the model should be later this year.

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Chemistry and Transport in a Multi-Dimensional Model

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Research Objectives

The focus of our research program is the achievement of a quantitative understanding of the spatial distribution and temporal variation of chemical species in the terrestrial atmosphere. Our activities aim at integrating the information obtained by spacecraft observations and contribute to a refinement of model descriptions of chemical, radiative and dynamical processes that are needed for realistic evaluations of man's impact on the global environment. A unique feature of our research effort is a close interaction between investigators at Caltech and JPL, including the laboratory chemical kinetics, the field measurement and modeling groups at JPL. Our research program has been directed towards three primary scientific goals: (a) the role of radiation and photochemistry in the lower stratosphere; (b) the rate of mass exchange between the troposphere and the stratosphere; and (c) the interaction between the atmosphere and the biosphere. Important secondary goals have been the confirmation of the chemical mechanisms comprising current models of atmospheric photochemistry such as NO_x and ClO_x partitioning, tropospheric ozone changes, and paleoclimate.

Summary of Progress and Results

Balloon profiles of stratospheric NO_2 and HNO_3 for testing the heterogeneous hydrolysis of N_2O_5 on sulfate aerosols: Simultaneous *in situ* measurements of NO_2 and HNO_3 agree well with gas-phase model calculations near 34 km (little aerosol present), but do not agree well at 24 km when there was high aerosol loading. When heterogeneous hydrolysis is included in the model computations, good agreement between measurements and model results.

In situ measurements of the NO_2/NO ratio for testing atmospheric photochemical models: The daytime NO_2/NO ratio determined from simultaneous *in situ* measurements is on the average lower than model results constrained by the *in situ* measurements. This demonstrates the need for

improved laboratory measurements of NO + O_3 and the NO_2 photolysis cross-sections at low temperatures.

Balloon observations of organic and inorganic chlorine in the stratosphere - The role of $HClO_4$ production on sulfate aerosols: High-resolution infrared solar observations of stratospheric organic chlorine and inorganic chlorine suggest a deficit in inorganic chlorine below 22 km which could be explained by the presence of $HClO_4$.

Hydrochloric acid and the chlorine budget of the lower stratosphere: In situ measurements of HCl in the lower stratosphere reveal that only 40% of inorganic chlorine is present as HCl, significantly lower than model predictions.

Heterogeneous reactions of $HNO_3(g) + NaCl(s) \rightarrow HCl(g) + NaNO_3(s)$ and $N_2O_5(g) + NaCl(s) \rightarrow ClNO_2(g) + NaNO_3(s)$: It is possible to convert salt (NaCl) to Cl_y in the stratosphere by reacting it with HNO_3 or N_2O_5. We propose that this might have happened immediately after the eruption of El Chichon in 1982.

Decadal evolution of the Antarctic ozone hole: Analysis of ozone column amounts obtained by TOMS during the late austral winter and spring for 1980-1991 show a distinct change after 1985 in the vortex averaged column ozone depletion rate during September and October.

Radiative forcing of the stratosphere by SO_2 gas, silicate ash, and H_2SO_4 aerosols shortly after the 1982 eruptions of El Chichon: An atmospheric radiative transfer model and observations have been used to estimate the amplitudes of the stratospheric radiative heating rate perturbations produced by stratospheric SO_2 and ash clouds injected by the El Chichon eruption.

The susceptibility of Antarctica to large increases in biologically damaging radiation after a volcanic eruption: Volcanic eruptions can inject large amounts of aerosol into the atmosphere, and, at large solar zenith angles, scattering by these aerosols can actually increase the flux of biologically damaging radiation reaching the surface.

ATMOS stratospheric deuterated water and troposphere-stratosphere exchange: Measurements of the isotopic composition of stratospheric water by the ATMOS experiment suggest that either the predominant source of water vapor to the uppermost troposphere is enriched convective water, most likely evaporated cloud ice, or troposphere-stratosphere transport occurs closely associated with tropical deep convection.

Methyl bromide - Ocean sources, ocean sinks and climate sensitivity: Using a simple steady state mass balance model, we have attempted to quantify the oceanic sources and sinks of CH_3Br. This analysis suggests that the open ocean is a small net sink. Furthermore, climate-induced variations in the atmospheric abundance of CH_3Br may be larger than those resulting from changes in the anthropogenic source.

Concentrations of tropospheric ozone from 1979 to 1992 over tropical Pacific South America from TOMS data: An estimate of tropospheric ozone concentrations was obtained from the difference in TOMS data between the high Andes and the Pacific Ocean. An increase in tropospheric ozone from 1979 to 1992 by 1.48 percent per year is consistent with the increase in biomass burning in the Southern Hemisphere.

Dust - A diagnostic of the hydrologic cycle during the last glacial maximum: The high level of dust concentrations in ice from the last glacial maximum can be explained if the strength of the hydrologic cycle during that epoch was about half of that at present. This is consistent with a large decrease in ocean temperature during that epoch as recently deduced from isotopic measurements in corals.

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ASSESSMENT, COORDINATION, MISCELLANEOUS

Development of JANAF Thermochemical Tables and Thermodynamic Data for Aqueous Solution Processes on Species of Importance to Ozone Depletion

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Research Objectives

The objective of the research effort is to provide accurate and internally consistent thermodynamic data on species involved in lower stratospheric, upper tropospheric homogeneous and heterogeneous reaction processes. The effort consists of two areas: (i) generation of Joint Army-Navy-Air Force Thermochemical Tables (JANAF) on selected gas phase species; and (ii) thermodynamic measurement of heat capacities of liquid-phase aqueous solutions. The results of this study will improve the accuracy of calculated equilibrium constants and other thermodynamic properties for reaction processes in the temperature range below 300 K.

Summary of Progress and Results

JANAF Thermochemical Tables

The thrust of the research effort during the period of 1994-1995 consisted of evaluation of spectroscopic and calorimetric data for the generation of JANAF Thermochemical Tables for numerous species including: (i) the reference species, $Br_{2(g)}$, $Cl_{2(g)}$, $I_{2(g)}$, $F_{2(g)}$, (ii) the oxides: $BrO_{(g)}$, $FO_{(g)}$, and $IO_{(g)}$, (iii) diatomics: $OH_{(g)}$, $HBr_{(g)}$, $HI_{(g)}$, (iv) interhalogens: $BrCl_{(g)}$, $IF_{(g)}$, $ClF_{(g)}$, $BrF_{(g)}$, and $Ibr_{(g)}$, and (v) polyatomic: $BrF_{3(g)}$, $F_2O_{2(g)}$, $FNO_{2(g)}$, $FO_{2(g)}$, $HOBr_{(g)}$, $BrNO_{2(g)}$, and $HOF_{(g)}$, (vi) carbon containing molecules: $BrCO_{(g)}$, $C_2H_2O_{2(g)}$, $C_2H_2O_{4(g)}$, $C_2H_3BrO_{2(g)}$, $C_2H_3ClO_{2(g)}$, $C_2H_4O_{3(g)}$, $ClCO_{(g)}$, $C_3N_2O_{(g)}$, $COBr_{2(g)}$, $COCl_{2(g)}$, $COF_{2(g)}$, $COI_{2(g)}$, $FCO_{(g)}$, $ICO_{(g)}$, $NC_2O_{(g)}$, $CH_4O_{2(g)}$, $C_2H_6O_{2(g)}$, $C_4H_6O_{4(g)}$.

Heat Capacities of Liquid-Phase Solutions

A differential scanning calorimeter, TA Instruments DSC 2920, was purchased in 1994 using NIST funds and is operational. The DSC 2920 with a liquid nitrogen cooling accessory operates at temperatures from 120 K to 750 K for cooling and heating scans. The differential scanning calorimeter, using closed pans to prevent vapor loss, is being used in a cooling scan mode enabling measurement of heat capacities of aqueous solutions in the liquid phase to temperatures far below the freezing point of these solutions. Thermodynamic data for supercooled aqueous solutions are necessary for calculation of standard-state properties leading to knowledge of equilibrium constants for mixed-solute systems and accurate determination of values such as vapor pressures of the acids gases over supercooled acid aerosol droplets.

Uncertainty of heat capacity results using DSCs has been typically 1 to 2% or larger. Refinement of low temperature and heat-flow calibration and heat capacity measurement techniques using differential scanning calorimeters has been completed. Initial testing and technique development were performed with water. The uncertainty of heat capacity results of water using the refined techniques were 0.3% from 300 K to ~20 K below the freezing point. Testing also was performed using emulsified water similar to the recipe published by Angell *et al. [J. Phys. Chem., 86,* 998 [1982]]. The water was dispersed in n-heptane using sorbitan tristearate as the organic surfactant to prevent coalescence of the water droplets. The majority of droplets were ~1-3 μm in diameter. The liquid-phase droplets were able to be supercooled about 40 K below the freezing point before crystallization began. The uncertainty of heat capacity results of the droplets were estimated as 0.75%. These techniques enable heat capacity measurement of dilute solutions to even lower temperatures. These measurements also clearly showed that supercooled solutions with droplet sizes similar to those found in atmospheric aerosols can exist. Heat capacity measurements of aqueous sodium chloride and sodium nitrate solutions for the Army recently have been completed with uncertainties as stated above for water showing the developed techniques work equally well for aqueous solutions.

Current work being done in 1996 consist of measurement of the heat capacities of aqueous hydrochloric and nitric acids from 180 to 300 K. Cost-effective DSC pans (sample containers) resistant to these acids had to be developed. These pans are basically commercially available stainless-steel sealable capsules which have been nickel, and then gold-plated. The capsules are reusable with a gold o-ring seal being replaced when necessary to maintain the seal.

Publications

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Data Survey and Evaluation

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Research Objectives

This task supports JPL participation in the NASA Panel for Data Evaluation. The purpose of the task is to maintain an updated set of evaluated rate constants and photochemical cross sections for use in stratospheric modeling, and to publish the evaluated data in a form accessible to the community of atmospheric scientists.

Panel Members	*Affiliation*
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Summary of Progress and Results

Evaluation Number 11 was published in December 1994. New reference software was implemented in that edition, as well as improved formatting methods to make data access more convenient. Preparations have begun for publication of the 1996 edition of the atmospheric data compilation, which will be Evaluation Number 12. A Panel meeting was held in May 1996 to survey new data and discuss proposed changes in the recommendations.

Publications

A series of eleven evaluations have been published since 1977, the most recent being Evaluation Number 11, JPL Publication 94-26, December 1994.

Chemical Kinetics Data Evaluation Activities

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Research Objectives

To provide the reliable, evaluated reaction rate database required as input data for large-scale modeling efforts which provide the basis for our understanding of atmospheric chemistry.

Summary of Progress and Results

The principal investigator has participated in the data evaluation activities of the NASA Panel for Data Evaluation on which panel he has the primary responsibility to review and evaluate the rate data for reactions of halogen-containing species. Updated and reevaluated databases were presented at meetings of the Data Panel.

The principal investigator also participated in the data evaluation activities of the IUPAC Commission on Chemical Kinetics Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Updated and reevaluated databases were presented at meetings of the Subcommittee.

Publications

Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, M. J. Rossi, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement V:, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, *J. Phys. Chem.*, accepted for publication, 1996.

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Electronic Dissemination of Global Emissions Inventories and Related Information on the World Wide Web

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Research Objectives

The Global Emissions Inventory Activity (GEIA) is a component of the International Global Atmospheric Chemistry (IGAC) Project. The ultimate goal of GEIA is to produce emissions inventories for all trace species from both anthropogenic and natural sources that are involved in global atmospheric chemistry. The GEIA Data Management and Communication Center, located in Boulder, Colorado and directed by Science & Policy Associates, Inc. is responsible for:

- Organizing and coordinating data management
- Coordinating inventory distribution and documentation strategies
- Organizing and maintaining a formal GEIA communication network
- Administering workshop planning and arrangements
- Setting up and overseeing distribution of GEIA data and documentation
- Facilitating participation in GEIA by inventory development experts.

In early 1996, NASA sponsored the development of a GEIA home page that is accessible via the World Wide Web (WWW). This electronic publication medium makes GEIA data, updates, workshop reports, and other information easily accessible to the GEIA community via the Internet.

Summary of Progress and Results

The project tasks were:

- Manage the project and maintain liaison with the GEIA Data Management Project Committee
- Learn Hypertext Markup Language and methods for linking to other Web pages
- Design and create Web pages
- Arrange access to a Web server
- Put the pages on the Web
- Create links to related Web sites

These tasks were completed successfully and the GEIA home page was established with support provided for this project by NASA Langley Research Center. Access to an existing Web server

site was provided by the University of Michigan at no cost to GEIA. The URL is <http://blueskies.sprl.umich.edu/geia/>. Expansion, maintenance, and updating of the GEIA Web site will be supported through the GEIA Data Management and Communication Center operating budget. Requests for continuing support are being pursued through NASA and NSF.

Publications

The NASA sponsored GEIA Web Site activities were reported at the June 1996 GEIA Workshop in Toronto. Other publications are planned.

Biogeochemical Cycling of Methyl Bromide and Related Halomethanes

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Research Objectives

Certain halocarbons present in the atmosphere contribute to global warming and the degradation of stratospheric ozone. The tropospheric residence times (J) for these halocarbons (e.g., CFCs, HCFCs, HFCs, and methyl halides) are usually calculated from the kinetics of their oxidation by reaction with hydroxyl radicals. These calculations, therefore, ignore the possibility that the Earth's biosphere may act as an additional sink for these substances. Hence, microorganisms present in both soils and natural waters may degrade these substances and thereby lower estimates of J. The goal of this research project is to determine if halomethanes can be degraded by bacteria present in soils, sediments, and natural waters, and to define the mechanisms by which these reactions proceed and to elucidate factors which speed or slow the reactions. The work focuses upon methyl bromide, but studies have been extended to dibromomethane, bromoform, and HCFCs like dichlorofluoromethane (HCFC-21) and difluorochloromethane (HCFC-22). The work encompasses both field and laboratory components. Fieldwork studies the dynamics of these reactions in estuaries, salt marshes, alkaline lakes, and in agricultural soils fumigated with methyl bromide. Laboratory work consists of delineating pathways using field materials and bacterial cultures.

Summary of Progress and Results

1994: The degradation of methyl bromide (MeBr) in anoxic sediments was investigated. MeBr undergoes a nucleophilic substitution reaction with sulfide, forming methane thiol, which was able to further react with MeBr to generate dimethyl sulfide. The linkage to bacterial degradation was at this level. The analogue ^{14}C-methyl iodide was used to follow pathways of degradation and the products were ^{14}C-methane and ^{14}C-carbon dioxide. Hence, MeBr is readily degraded in anoxic environments, provided that free sulfide is present.

The aerobic degradation of MeBr was studied. MeBr was degraded by methanotrophs, however methane is a competitive inhibitor of the oxidation. Studies with soils indicated that bacteria other than methanotrophs (or nitrifiers) can oxidize MeBr to carbon dioxide. Some soil experiments were carried out in the low ppm range, which was the first evidence that soil bacteria could degrade trace levels of this compound.

Trifluoroacetate (TFA) is a stratospheric oxidation product of certain HCFCs and HFCs which is thought to be resistant to biodegradation. In anoxic environments the compound underwent a

sequential defluorination which eventually yielded acetate. Acetate was further degraded to methane or carbon dioxide. Under aerobic conditions, the evolution of fluoroform was detected.

Various HCFCs were found to be metabolized by methanotrophic bacteria in aerobic soils. Anaerobic soils gave evidence of reductive dehalogenation carried out by bacteria. These reactions proceeded at low ppbv levels implying that bacteria could degrade these substances at realistic atmospheric mixing ratios.

1995: Field investigations were conducted on MeBr-fumigated strawberry fields. An increase in soil gas content of methane and nitrous oxide was detected, because of the inhibition of methane oxidation, nitrification, and nitrous oxide reduction by MeBr. Oxidation of MeBr was greatest during fumigation, when soil MeBr levels were highest. The bacteria responsible for this activity are as yet unknown, but if they can be stimulated, then outward flux of MeBr can be constrained.

Shoreline bacterial mats from Mono Lake, CA rapidly metabolized MeBr to methane and carbon dioxide. MeBr was oxidized by water column bacteria, but neither methane oxidation nor nitrification were linked. Indications are that trimethylamine-using methylotrophic bacteria were the agents responsible for the bulk of the MeBr degradation.

1996: The bacterial oxidation of dibromomethane and bromoform are being studied in natural waters. The enhancement of MeBr oxidation in soils is being investigated. The inhibitory effect of various HCFCs and methyl halides on methanotrophic bacteria was followed to determine the mechanism by which they oxidize halomethanes.

Publications

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Upper Atmosphere Data Pilot

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Research Objectives

Rapid, effective access to the increasing volume of data on trace gases is important in advancing our knowledge of the Earth's atmosphere. This task provides development, operation, and maintenance of an electronic database for such atmospheric data with emphasis on 2-D datasets from models and satellite measurements and on selected aircraft and ground-based datasets. The database serves the atmospheric science community by providing convenient access to data, by providing data manipulation and display services, and by supporting special intercomparison and atmospheric assessment activities. This work is complementary to the measurements and models database effort under the Atmospheric Effects of Stratospheric Aircraft (AESA) Program funded through the NASA High Speed Research Program (HSRP).

Summary of Progress and Results

A major effort under this task has been working with the Models and Measurements (M&M) Committee of the AESA program. Revised data from modeling groups participating in the M&M intercomparison activity were incorporated into the database. Analyses and plots of the data were prepared for the M&M workshop report published in 1993. A compact disc containing the report and data was also produced and distributed in 1994.

We continued efforts to incorporate existing and updated measurements from satellite experiments and other missions into the database with emphasis on the troposphere and lower stratosphere. Work was begun in conjunction with NASA's Global Troposphere Experiment (GTE) Project and the Langley Research Center Earth Observing System Digital Active Archive Center to incorporate selected GTE field experiment data, with emphasis on measurements of ozone, carbon monoxide, and nitrogen species. Both aircraft-and ground-based measurements of the troposphere and lower

stratosphere were added. Other existing and updated model and measurement data as were added and processed as required to support assessment and intercomparison activities such as the Intergovernmental Program on Climate Change (IPCC) and the 1994 ozone assessment of the United Nations Environment Programme and the World Meteorological Organization.

As support from the Atmospheric Chemistry and Modeling Program was ending in 1994, we began a major database development effort in support of High Speed Civil Transport (HSCT) assessment activities under the AESA program. A series of aircraft emissions scenarios were developed using emissions data compiled for various classes of aircraft by Boeing and McDonnell Douglas. These emission scenario datasets are available on both 3-D (longitude, latitude, altitude) and 2-D (latitude, altitude) grids and include cases for 1990 and 2015 subsonic fleets and for potential Mach 1.6 and Mach 2.4 HSCT fleets. The data were assembled on the UADP system, regridded to the model grids of six AESA modeling groups, and distributed for use in HSCT assessment modeling runs. Resulting model projections were incorporated into the database, and plots and analyses of the data were provided to the modelers and authors of chapters of the HSRP program report. Revised model projections submitted to the database subsequent to the 1993 Interim Assessment meeting were also analyzed, plotted, and provided for the program report.

Other significant efforts have involved distribution of the aircraft emissions scenario data to the scientific community. A presentation was made at the HSRP/AESA annual meeting describing the data and advertising its availability. The emissions scenario datasets, color plots of the data, and summary tables were made available to users for electronic access. As of the end of FY 1994, the data had been provided to more than 25 users from government agencies, universities, and industry.

Efforts continued to keep hardware capabilities current. A new color printer was added to enhance color graphics output capability. Also, the database workstations were upgraded in both memory and processing speed.

Publications

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Analysis of ATLAS-UARS Coincident Measurements

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Research Objectives

A major goal of the Atmospheric Laboratory for Applications and Science (ATLAS) program is to achieve underflights of the Upper Atmosphere Research Satellite (UARS) to obtain correlative measurements between the two missions. The UARS carries a variety of scientific instrumentation for studying the composition and dynamics of the atmosphere. The ATLAS instruments obtain extensive observations of the Earth's atmosphere. The combination of the results from the UARS and the complementary atmospheric measurements from the ATLAS experiments will greatly advance the understanding of the chemistry of the upper atmosphere. Maximum use of the two satellite datasets will be provided when near-coincident (correlative) measurements are obtained. The objectives of this research are to: (1) provide pre-launch predictions of correlative measurement opportunities between instruments on the two satellites in order to establish or evaluate ATLAS launch time; (2) provide real-time mission support to predict the time and location of correlative measurements for use in developing operations schedules for the ATLAS instruments; and (3) determine correlative measurement opportunities based on actual orbits and instrument operation times for use by the scientific community. An additional objective is to provide overflight data for each of the ATLAS 3 instruments for selected ground sites making atmospheric observations.

Summary of Progress and Results

A comprehensive computer simulation study was performed to define coincident measurement opportunities between ATLAS 3 atmospheric experiments (ATMOS: Atmospheric Trace Molecule Spectroscopy, MAS: Millimeter-wave Atmospheric Sounder, CRISTA: CRyogenic Infrared Spectrometers and Telescope for the Atmosphere, MAHRSI: Middle Atmosphere High Resolution Spectrograph Investigation, and SSBUV: Shuttle Solar Backscatter UltraViolet) and UARS experiments (HALOE: Halogen Occultation Experiment, and MLS: Microwave Limb Sounder). This simulation study provided information, both in tabular and graphical form, on geographical and temporal coverage of the various experiments for correlative and data validation studies. These results also established the optimum launch time and date for the ATLAS 3 mission to obtain correlative measurements with UARS.

The correlative measurements prediction team participated in pre-launch mission simulations. Based on ATLAS 3 orbital parameters supplied by mission control, quick-response simulation results were provided for coincident measurement opportunities between instruments on the two satellites. Tabular results were sent electronically, and plotted results were faxed. The mission simulation demonstrated that the computations could be made in a timely fashion for supporting mission operations decisions.

ATLAS 3 was launched on 3 November 1994; the mission length was approximately 10 days and 22 hours. Real-time mission support was provided to predict when and where correlative measurements between ATLAS 3 and UARS would occur. ATLAS 3 orbit elements were updated three times during the mission, and the correlative measurement predictions revised as appropriate. Geographical coverage predictions were provided for the selected ATLAS 3 and UARS instruments. Correlative opportunities were determined for the various instrument combinations on the two satellites. Tabular results included Greenwich time, mission elapsed time, satellite position, viewing geometry, geographical location of the measurement point, and time and distance between the measurement points of the two instruments. All data were provided to the mission operations team and used to develop instrument operating schedules. In addition, overflight times were determined for each of the ATLAS 3 instruments at ground sites including Kislovodsk, Lake Issyk-Kul, Tomsk, Yakutsk, Moscow, Zvenigorod, Heiss Island, Ny-Ålesund, Jungfraujoch, Table Mountain, Kitt Peak, Fritz Peak, Thule, Mauna Loa, Reunion Island, Lauder, and Dumont d'Urville. These data were provided to the mission operations team and to scientists at the ground sites.

Following the mission, the instrument operations schedule and the Space Shuttle attitude summary were used to develop a database of actual correlative measurement opportunities between the various instruments. The results were documented in a NASA report.

Publications

Harrison, E. F., F. M. Denn, and G. G. Gibson, *ATLAS 3 Correlative Measurement Opportunities With UARS and Surface Observations,* NASA Technical Memorandum 110159, June 1995.